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Application of advanced technologies for CO_2 capture from industrial sources

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Abstract

The great majority of the research on CO_2 capture worldwide is today devoted to the integration of new technologies in power plants, which are responsible for about 80% of the worldwide CO_2 emission from large stationary sources. The remaining 20% are emitted from industrial sources, mainly cement production plants (~7% of the total emission), refineries (~6%) and iron and steel industry (~5%). Despite their lower overall contribution, the CO_2 concentration in flue gas and the average emission per source can be higher than in power plants. Therefore, application of CO_2 capture processes on these sources can be more effective and can lead to competitive cost of the CO_2 avoided with respect to power plants. Furthermore, industrial CO_2 capture could be an important early-opportunity application, or a facilitate demonstration of capture technology at a relative small scale or in a side stream.
This paper results from a collaborative activity carried out within the Joint Programme on Carbon Capture and Storage of the European Energy Research Alliance (EERA CCS-JP) and aims at investigating the potentiality of new CO_2 technologies in the application on the major industrial emitters.

1. Introduction

The great majority of the research on CO_2 capture worldwide is today devoted to the integration of

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new technologies in power plants, which are responsible for about 80% of the worldwide CO_2 emission from large stationary sources. The remaining 20% are emitted from industrial sources, mainly cement production plants (~7% of the total emission), refineries (~6%) and iron and steel industry (~5%) [1]. Despite their lower overall contribution, the CO_2 concentration in flue gas and the average emission per source can be higher than in power plants. Therefore, application of CO_2 capture processes on these sources can be more effective and can lead to competitive cost of the CO_2 avoided with respect to power plants. Furthermore, industrial CO_2 capture could be an important early-opportunity application, or facilitate demonstration of capture technology at a relative small scale or in a side stream. It should also be highlighted that in some countries, industrial sources may be responsible for high fractions of the total emissions, especially where low-carbon sources like nuclear (e.g. in France) and renewables (e.g. in Scandinavian countries) provide a large share of the total power supply.

This paper results from a collaborative activity carried out within the Joint Programme on Carbon Capture and Storage of the European Energy Research Alliance (EERA CCS-JP) [2]. Firstly, the source of emission and the main characteristics of the gaseous streams candidate for CO_2 removal in cement, refineries and iron & steel plants are summarized. Then, the potential of the different CO_2 separation processes are evaluated for each case, with particular attention for the most advanced technologies today under development.

Only cement plants, iron and steel plants and refineries are considered in this study due to their primary contribution to the total world emissions. However, many other CO_2 emission sources deserve attention for future installations for CO_2 capture [3,4]. High-purity industrial sources, such as natural gas processing, hydrogen production, coal/gas-to-liquids and ammonia production, currently supply the majority of the CO_2 that is injected in CO_2 storage demonstration projects. Pulp and paper industry can account for significant biogenic CO_2 emissions in certain areas. The production of biofuels, both through bio-chemical and thermo-chemical conversion, typically also results in a high-purity CO_2 stream. At present approximately 1 Mt of CO_2 per year is captured at the Archer Daniels Midland Company corn-based bio-ethanol plant in Decatur, Illinois, and injected in the Mount Simon Sandstone saline formation as part of an elaborate CO_2 storage measurement, verification, and accounting program [5]. The production of biofuels with CCS could lead to net negative emissions; i.e. carbon is sequestered in biomass from the atmosphere therefore the use of biofuels offsets CO_2 emissions of fossil fuels, while most of the remaining carbon ends up in high-purity CO_2 streams that can be captured and stored [6]. The capture CO_2 from high-purity sources and biofuels production processes only affects the thermal efficiencies of these processes to a minor extent, unlike CO_2 capture at power plants. Additional operating and capital expenditure typically only involves CO_2 drying and compression, which reduces the overall CO_2 avoidance costs significantly in comparison with CCS during electricity generation.

2. Cement industry

Due to the high amounts of fossil fuels utilized during cement manufacture processes and the release of CO_2 from calcination of carbonated materials ($CaCO_3$ and $MgCO_3$) in the raw materials, cement plants are responsible for the highest emissions among the industrial sources other than power generation, even after improvements in energy efficiency [7]. Cement plants are characterized by a single source of emission (the cooled flue gas from the preheater), characterized by CO_2 concentrations of 15-30%, typically released to the environment from one or two emission points, after providing heat for raw material drying.

2.1. Potential application of CO_2 capture technologies

From 50 to 70% of CO_2 emissions from cement plants originate from the calcination of carbonated materials, the remaining fraction being associated to the oxidation of carbon in the fuel. For this reason, fuel decarbonization by pre-combustion capture processes is not effective in reducing the emissions from cement plants and research is focused on post-combustion and oxyfuel combustion processes.

In the case of oxy-combustion, oxygen mixed with recycle CO_2 is fed to the burners instead of air. There are two locations in a cement plant where combustion takes places; the pre-calciner, where fossil fuel or wastes are burnt to reach calcination temperature of ~900°C, and the kiln where cement clinker is produced at 1450°C. Oxy-combustion in the pre-calciner is suggested as a viable option to capture CO_2 from fuel combustion and raw material calcination, avoiding technical uncertainty of operating the cement kiln under oxy-combustion conditions [8]. Dual preheaters with oxy-combustion pre-calciner have been designed while raw mill, kiln and clinker cooler operate conventionally. Part of the CO_2-rich flue gases from the pre-calciner is recycled back and mixed with oxygen to prevent excessive flame temperatures. The CO_2 avoidance rate by oxy-combustion in pre-calciner is 61% since only part of the CO_2 can be captured. ECRA [9] has been investigating the operation of the cement kiln as well as the pre-calciner under conditions of oxy-combustion for new installed cement plants. The theoretical and experimental outputs of this new design would allow utilization of oxy-combustion in the kiln, resulting in higher CO_2 avoidance rates. The applicability of advanced oxygen production technologies, such as oxygen transport membrane-based systems (OTM), should be investigated to reduce energy and economic penalties involved in conventional cryogenic air separation which would reduce the energy consumption of oxy-combustion further. However, since OTM are best coupled with a combustion turbine providing hot and high pressure air [10], it is reasonable that a combined cycle power plant would be needed for OTM integration. Therefore, allocation of additional CO_2 emissions from fuel combustion to the cement plant should be accepted, or a decarbonized fuel should be used in the turbine, bringing about additional cost and plant complexity.

Post-combustion CO_2 capture represents the alternative option for end-of-pipe CO_2 abatement and provides low technical risk. The high CO_2 concentration in the flue gas would make amine-based post-combustion absorption attractive for the cement industry. However, a significant amount of steam is required for solvent regeneration and this is expected to have high energy penalties since a separate steam boiler is needed to supply steam to the solvent regeneration stripper (in case of capture rates > 80%, only 10 to 50% of the heat required for solvent regeneration can be recovered from the plant waste heat [11]). The steam generator could generate some electricity with one back pressure turbine as well as steam [8]; however, such a steam cycle design results in very low plant efficiency. The integration of an amine process with a cement plant, capturing the CO_2 from the flue gases from the raw mill has been investigated in [8]. A coal-fired CHP plant has been designed to provide the steam for solvent regeneration. The flue gases resulting from fuel combustion in the CHP plant is also fed to the amine process. The need of flue gas desulphurization (FGD) and selective catalytic reduction (SCR) units are major limits of this configuration, in which up to 85% of the released CO_2 can be captured, corresponding to 74% of CO_2 emission avoided. Therefore, the application of the advanced solvents systems, requiring less energy consumption for carbon capture than an amine process and having improved tolerance to SO_x and NO_x, deserves to be investigated further. Similarly, advanced post-combustion capture technologies based on physical processes (e.g. advanced solvents, sorbents, CO_2 membranes) could be applied successfully in cement plants.

Calcium looping (CaL) process can be a promising post-combustion capture technology especially when integrated with cement plants. The process operates between two reactors: one is the carbonator in which CO_2 is captured by exothermic carbonation reaction at ~650 °C and the other is the calciner where $CaCO_3$ is regenerated to CaO by endothermic calcinations reaction. Since the process operates at higher temperatures than the amine process and uses CaO, which is one of the cement raw materials, it is more

advantageous to apply this process to cement plants. This is because the purge from the calciner can be used as additional feed for clinkerization [12]. In addition, the heat of the carbonation reaction can be recovered by generating steam for a steam cycle and the integration of the Ca-looping process on different locations of the cement process can be implemented without additional heat exchange requirements. Rodriguez et al. [13] applied this process to the kiln gas and achieved up to 99% capture rate. The raw material including $CaCO_3$ and $MgCO_3$ has been calcined in a retrofit oxy-calciner replacing the existing pre-calciner. While part of the raw material from the oxy-calciner is sent to the kiln for cement production, the rest is fed to the carbonator to capture CO_2 resulting from fuel combustion in the kiln. The Ca-looping process can be applied to 3rd preheater stage [14]. This location provides higher CO_2 concentration and lower volumetric gas flow rate. It was suggested that CO_2-depleted flue gases from the carbonator is routed back to 2nd preheater stage for additional raw material preheating. It has been reported that this process is capable of reducing CO_2 emissions by more than 90%. In both designs, the surplus energy is recovered and used for electricity generation, achieving lower energy penalties. Another possibility is a symbiosis model of a power plant, a cement plant and a CaL process, where the flue gases of both plants [15] or the power plant only [16] are treated in the CaL unit. It must be highlighted that co-location of the power plant and the cement plant is needed in these cases, since transporting large amounts of solids between the two plants over long distances would bring about additional costs and logistic issues.

Another advanced CO_2 capture option for cement manufacture is to separate combustion and calcination occurring in conventional pre-calciner into two different chambers [17]. Therefore, the pre-calciner consists of a calciner and CFB combustor at 1056°C. The calcium oxide, which is used as heat carrier is transferred between the combustor and calciner. The calciner operates at 937°C, and the heat requirement in the calciner due to endothermic calcination reaction and fresh sorbent preheating can be supplied by preheated CaO coming from the combustor. The CO_2 capture rate is lower compared to post-combustion capture since it cannot recover the CO_2 generated by fuel combustion. Therefore, this option is only usable when the target is moderate level of CO_2 reduction.

3. Iron & Steel industry

Integrated steel mills based on blast furnace (BF) and basic oxygen furnace (BOF) route, the most common iron production process around the world, are characterized by plants with very high average emissions per installation. Averagely, 3.5 $MtCO_2$/year are emitted by integrated steel mills, vs. 3.9 $MtCO_2$/year of coal-fired power plants and 1 $MtCO_2$/year of natural gas-fired ones [1]. This process requires a powerful reducing agent to reduce iron ore. The main carbon input to the steelmaking process is coke utilized in the blast furnace process. The coke utilized in the process can be either bought or produced on site. The side product from the blast furnace process is blast furnace gas, a CO-rich low-BTU gas that is utilized on the steel mill site as an energy carrier. As the blast furnace gas, which contains 50-80% of the total carbon entering the steel mill in the form of CO and CO_2, is utilized on site, e.g. for pre heating of the hot blast or at a power plant, it is the source of majority of the CO_2 emissions. In addition, production of coke results in carbon-rich coke oven gas and finally CO_2 emissions. Numerous improvements, such as energy efficiency improvements and new process configurations enabling alternative fuel usage, in complicated BF+BOF based steel mills are possible, but the reductions in CO_2 emissions are typically small in comparison to overall CO_2 emissions from the mills and the possibilities of CO_2 capture technologies. Most of the iron and steel installations in Europe are old mill sites and therefore would be considered as retrofit installations, either with post-combustion capture or other technologies in relation to the blast furnace lifecycle.

There is no single one typical configuration for an integrated iron and steel mill. Some process steps,

e.g. coking or sintering can be outsourced or centralized. Different options for integrating different processes in and outside plant site can be considered. The main integrations between process units are based on flexible and efficient utilization of process gases in processes, direct heating and power and heat production. Despite the different configurations and process units on site, the CO_2 emissions are typically scattered into several stacks around the mill site of several kilometers in diameter. This poses a challenge for the capture of CO_2. However the main sources of CO_2 can be identified.

The carbon dioxide can be captured from an iron and steel integrated plant either from the combustible process gases or flue gases coming from combustion of process gases and other fuels. The fuel mixes of the mills can vary significantly therefore it is very difficult to provide typical flue gas compositions and impurity levels. Some indicative values are however reported in Tab. 1.

Tab. 1 Indicative characteristics of the gas streams relevant for CO_2 capture in an integrated iron and steel mill. Data from [18-20].

Relevant streams	Concentration of carbon species, % v/v	Other component and impurities	% of total emissions
Power plant flue gas *	Boiler: 15-25 Combustion turbine: 7-12	O_2, N_2, SO_x 10-30ppm, NO_x 30-60ppm	40-70
Hot Stoves flue gas	CO_2: 15-25	O_2, N_2, SO_x 10-30ppm, 30-60ppm	15-30
Lime kiln	CO_2: 20-30%	O_2, N_2, low NO_x, low SO_x	2-5
Coke plant flue gas	CO_2: 15-25%	O_2, N_2, high NO_x	15-20
Sinter plant	CO_2: 5-10%	O_2, N_2, Dust, SO_2, Dioxins, Heavy metals, NO_x	5-20
Blast furnace gas	CO_2: 20-25 CO: 20-25 C_nH_m: <1	H_2, N_2, dust	-
Coke oven gas	CO_2: 2-5 CO: 4-7 C_nH_m: 20-50	H_2, N_2	-
Basic oxygen furnace gas	CO_2: 10-18 CO: 55-80	H_2, N_2, dust,	-

* Normally the power plants use a mixture of fuels, often including imported natural gas. Therefore, the variability of the power plant flue gas is particularly large.

3.1. Potential application of CO_2 capture technologies

The conventional post-combustion capture technologies are in general suitable for capture of CO_2 from steel industry installations. The varying characteristics of different gas streams pose a challenge for installation of capture units. SO_x, NO_x and dust can require additional gas cleaning before the capture unit. Also the varying sizes, composition and location of different streams challenge the installation aiming at high CO_2 capture levels. Advanced post-combustion processes may however be successfully applied on steel mills flue gases, especially if requiring low regeneration heat and showing a high tolerance toward the impurities in the stream to be treated.

In addition to the post-combustion capture technologies, pre-combustion capture techniques can also be applied on fuel gases to produce a H_2-based gas to be used in the power plant and the main process heaters (hot stoves and coke plant). In particular, pre-combustion processes may provide higher carbon capture rates in the power plant. As a matter of fact, due to the high carbon content and the low heating value of the BFG (by far the main fuel typically used in the power plant), the steam produced in an advanced combined cycle may not be sufficient for high capture levels. Thus, the advanced pre-combustion technologies for CO_2 separation (e.g. SEWGS, CO_2 membranes) can have interesting potential in this application [21]. Conversely, pre-combustion technologies featuring H_2 separation (e.g.

H_2 membranes) are not suitable for application on BFG, which is a N_2-rich gas and would hence leave a highly diluted CO_2 stream.

In addition to processes which does not affect the blast furnace, several options changing the blast furnace process have also been considered. All of these are resulting with gas stream with higher concentration of CO_2 than conventional blast furnace. The CO_2 will further have to be separated e.g. with PSA or with adsorption process, but with a smaller cost, due to the high partial pressure of CO_2. Oxygen blast furnace is one of the improved blast furnace processes with the CO_2 separation phase needed, in order to maintain a high utilization ratio of carbon input. When considering capture of CO_2, oxygen blast furnace and Top Gas Recycling (TGR) are ways to increase the CO_2 partial pressure in the off gas [22]. The capture of CO_2 from the off gas can be done e.g. with PSA or chemical adsorption.

Advanced oxygen production processes like OTM may be successfully employed in integrated steelworks with TGR configuration. However, it must be highlighted that TGR configuration reduces the availability of fuel gas, so that a gas turbine cycle integrating OTM should use a fuel provided externally from the steelworks, which should be properly decarbonized to avoid additional emissions.

Steelmaking processes, alternative to blast furnace, are also under investigation [22]. Direct reduced iron (DRI) is an alternative iron making processes based on the direct reduction of iron by a H_2 and CO-based reducing gas, making CO_2 capture a part of the process enhancement measures. DRI is currently utilized without CO_2 capture in smaller installations generally using large amounts of scrap iron as raw material instead of iron pure ore. Pre-combustion technologies can be here integrated for CO_2 capture. FINEX, an advanced smelting technology and HIsarna are also new types of processes replacing conventional blast furnace. FINEX process utilizes iron ore and non-coking coal instead of coke with multiple circulating fluidized beds. The CO_2 capture is based on pure oxygen feed and a flue gas circulation, with CO_2 removal step. The HIsarna process removes the need for producing pig iron in a blast furnace prior to the production of steel.

4. Refineries

Refineries are characterized by a number of unit processes and by a variety of possible configurations and levels of complexity. As a consequence, in refineries there are typically many emission points scattered over wide areas, each flue gas stream characterized by quite different compositions in terms of CO_2, O_2, SO_x, NO_x and other contaminants content. As shown in Tab. 2, most of the CO_2 emissions derive from fuel combustion in process heaters, utility boilers and power generation plants, followed by FCC and hydrogen plant. Other CO_2 emission sources are present in refineries (e.g. sulfur recovery processes, flaring), but their contributions account for a very small fraction of the total emissions share.

Due to the variety of processes in refineries, the possible new integration opportunities should be considered when assessing the application of CCS technologies for an optimal low emission and low energy consumption configuration. As a matter of fact, by including new processes for CO_2 capture new thermal integration options for waste heat recovery and new ways for the utilization of material streams (e.g. the use of carbon-rich PSA off-gas in a CLC boiler) may arise. Many integration opportunities will also arise between the refinery unit operations and the power plant. For example, the adoption of a polygeneration plant based on fuel gasification, efficiently integrating units for the separation of hydrogen and oxygen to be exported to other refinery processes, while producing decarbonized heat and power, might provide important benefits.

In EU and most of the developed countries, it is expected that most of the CCS installations will concern retrofitting applications. Therefore, the suitability of the new technologies for retrofitting is an important point. However, new unit operations may also rise in existing refinery complexes. For example, new hydrogen plants may be expected considering the increasing H_2 demand for hydrotreating and

hydrocracking processes. Similarly, new advanced power plants may be built under proper conditions of the power market (e.g. as happened with the four IGCCs fed with oil heavy residues recently built in Italy [23]).

Tab. 2 Characteristics of the refineries streams relevant for CO_2 capture. Data from [24-27]
* electricity and steam generation
** in case of solvent based purification
*** if syngas from residue gasification, higher CO_2 concentrations, higher pressures, and also H_2S and COS in syngas

Relevant streams	CO_2 concentration, %v/v	Other component and impurities	% of total emissions
Process heaters and utilities* flue gas	Gas-fired: 3-6 Oil fired: 7-12	O_2 (2-6%v/v), SO_2 (gas-fired: 10-20 ppmv, oil-fired: 50-600 ppmv), SO_3, NO_x	Process heaters: 30-60 Utilities: 20-50
Fluid catalytic cracker flue gas	8-12	O_2 (1-2%v/v), SO_2 (1000-15000 ppmv), catalyst dust, CO, SO_3, NO_x	20-35
H_2 production plants: Syngas*** PSA off-gas Regenerator off-gas** FTR furnace flue gas	15-35 (@ 20-30 bar) 40-50 95-99 5-20	H_2, CO, CH_4, N_2 H_2, CO, CH_4, N_2 Traces O_2 (2-6%v/v), NO_x	- - - 5-20

4.1. Potential application of CO_2 capture technologies

All the three concepts (post-combustion, pre-combustion and oxyfuel) have been considered in the literature for CO_2 capture form refineries [11,24,25,28,29], with MEA-based absorption as reference technology. In all the studies, a centralized CO_2 capture plant has been considered for economic reasons, requiring a large piping network and compression power on flue gas. Issues concerning the rather low CO_2 concentration in flue gas, the degradation resulting from contact with O_2 and the need of flue gas purification down to very low levels of SO_x (below 20 ppm), NO_x and PM, contribute increasing capital and operating costs. Further, most refineries' steam networks are constrained. Utilizing MEA-based absorption technology would require a large steam consumption that would, in most cases, not be feasible without a retrofit of the site utility system.

Innovative post-combustion processes, including advanced solvents, solid sorbents, CO_2 membranes, may represent an alternative to MEA-based absorption. Potentially these have a lower regeneration heat demand which would be a general benefit of these processes. Specific benefits in industrial processes may be obtained when capture agent properties are tailored for specific feed gas and process characteristics, such as composition or temperature levels (e.g. a specific solid sorbent or solvent may be developed for capture from dry feed gas). Besides, when contaminants are present, alternative to MEA-based process may be more attractive if they can handle and possibly remove he contaminants, for instance SO_x.

Among the post-combustion processes, calcium looping (CaL) can be mentioned due to its peculiar characteristics, which make it interesting if properly integrated with other unit operations. CaL process does not need a desulfurization plant, since the CaO sorbent in the carbonator can remove most of the SO_2 in the flue gas together with CO_2. While capturing CO_2, heat must be recovered in the carbonator, indirectly provided by the additional fuel burned in the calciner under oxyfuel conditions. Thus, possible integration opportunities with process heaters and the replacement of utility boilers should be considered. One drawback of the technology is the need of large supply of fresh limestone makeup and purge, which may be relevant especially in case of SO_2-rich flue gases and high sulfur fuel burning in the calciner, causing premature sorbent deactivation. This issue might however be limited if the CaO-rich purge is used for S-removal in a coke or heavy oil fluidized bed boiler or gasifier.

As far as oxyfuel is concerned, application on boilers seems easier than on process heaters, which pose additional challenges, especially for retrofitting, due to the lower standardization and the need to carefully control the flames heat release profiles [11,25]. In addition to boilers and heaters, the application in the FCC regenerator is promising and is currently being tested in a pilot installation in Brasil [30]. Due to the economies of scale of state-of-the-art cryogenic O_2 plants, such a concept would include a centralized ASU and a high purity oxygen piping network.

Oxyfuel processes may take advantage from the development of advanced O_2 production technologies. Cryogenic air separation units (ASU) are at present the only mature technology capable of supplying oxygen at the purity and scale required for oxyfuel process. Attempts to improve this 100 year old technology are receiving increased attention [31]. Oxygen transport membranes, for example, might be integrated with the power plant and separate the oxygen from the high pressure air from the combustion turbine compressor. It must be noted that other non-CCS processes with O_2-blown reactors (e.g. heavy residue gasification, ATR) may take advantage from the development of oxygen membranes or other innovative O_2 production technologies.

Among the oxyfuel technologies, CLC based on atmospheric dual fluidized bed system appears very promising for process heaters and utility boilers. The level of development of such a system is also at a rather advanced stage with respect to other long term technologies, since continuous operations have been demonstrated in different pilot installations. An important advantage of this oxyfuel system is that it does not require the production pure O_2, eliminating issues associated to pure O_2 handling and delivery. It is important to note that CLC has been proven at laboratory scale on gaseous fuels, while the CLOU process for solid fuels oxidation is at an early stage of development and continuous operations still need to be demonstrated. Also combustion of liquid fuels still needs to be proven, since only preliminary tests have been carried out in few laboratory tests. The development of a process able to burn liquid fuels is of primary importance for refineries, since a large fraction of the fuels burned in process heaters and utility boilers is at the liquid state (typical gas to liquid fuel share in refineries ranges from 80/20 to 40/60%, with higher liquid fuel shares in the most complex refineries [27]).

Pre-combustion capture technologies are natural candidates for H_2 production plants. Advanced solvents, membrane reactors, SEWGS, SER, CLR may all be applied on H_2 plants. Technologies that, in principle, shift the equilibrium favourably and thus allowing reducing the pieces of equipment needed for fuel conversion (e.g.: H_2 membrane reactors, sorption enhanced reactors) and decreasing the reformer operating temperature (e.g.: H_2 membrane reformers, sorption enhanced reformers) provide additional benefits.

Processes producing high purity H_2 (e.g. dense membranes) are also favored since allow avoiding any H_2 purification steps like PSA. Similarly, processes capable of producing high pressure H_2 (e.g.: SEWGS, CO_2 membranes, some SER configurations, CLR) are also favored since they do not need the high power consuming H_2 compression. However, no advanced technology seems to be capable of producing both high purity and high pressure H_2 at the moment: H_2 membranes would require an abundant sweep steam to keep high absolute pressures on the permeate side, while CO_2 sorbents and CO_2 separators are not able to produce >99% purity H_2. Nevertheless, it must be said that the downstream PSA purification unit would benefit from a bulk CO_2 removal, since smaller flow rates would need to be treated and smaller size vessels would hence be required. High temperature pre-combustion separation processes (SEWGS, SER, CLR and high temperature H_2 and CO_2 membranes) potentially also lead to thermal integration benefits, since a significant amount of heating and cooling is avoided and better heat integration can be obtained.

Pre-combustion capture technologies have also been proposed for process furnaces and boilers, where H_2 is produced in centralized plants and distributed as decarbonized fuel by a piping network. Again, for an optimal overall efficiency, but also for safety reasons, integration with the power plant should be

considered and the adoption of a high efficiency CHP H_2-fired combined cycle generating decarbonized power should be considered.

5. Conclusions

The characteristics of the main industrial CO_2 emission sources have been briefly reviewed in this paper, considering the composition of the carbon-rich streams and their contribution to the total emissions. The possible application of the main CO_2 capture technologies has been considered for each source, with particular attention for mid-long term technologies today under development. A qualitative summary of the potentiality of these technologies, reflecting the opinion of the authors, is reported in Tab. 3 and shows that many of the processes, whose development is primarily focused on power generation applications, may be interestingly applied in other fields. Such an output can represent an input for better investigation of these applications, for both technology developers and final users.

Tab. 3 Qualitative evaluation of the potential of advanced technologies in CO_2 capture from industrial sources. The evaluation reflects the opinion of the authors and does not consider the level of maturity of the technologies, but assumes that a proper development is possible. Some evaluations are conditioned to a proper configuration and integration with other processes, as discussed in the text.

Technology	Cement	Iron & steel	Refineries		
			Process heaters & boilers	FCC	H_2 plant
Post-combustion					
Advanced solvents	+	+	+	+	-
Low temperature sorbents	+	+	+	+	-
Ca-looping	++	+	+	+	-
CO_2 membranes	+	+	+	+	-
Oxyfuel					
CLC	--	-	++		+
OTM	+/-	+/-	+	++	+ (ATR/CPO)
Pre-combustion					
Advanced solvents	--	+	+ (CHP)		+
H_2 membranes	--	--	++ (CHP)		+
SEWGS	--	+	++ (CHP)		+
SER	--		++ (CHP)		+
CLR	--		++ (CHP)		+
CO_2 membranes	--	+	++ (CHP)		+

References

[1] IPCC. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. : [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2005.

[2] European Energy Research Alliance (EERA). Joint Program on CCS. www.eera-ccs.eu. ;September 2012.

[3] UNIDO. Carbon Capture and Storage in Industrial Applications: Technology Synthesis Report. November 2010.

[4] IEA/UNIDO. Technology roadmap, Carbon capture and Storage in Industrial Applications. 2011.

[5] Midwest Geological Survey Consortium website. http://sequestration.org. ;October 2012.

[6] EBTP/ZEP. Biomass with CO_2 capture and storage (Bio-CCS) – The way forward. Brussels, Belgium, 2012;October 2012.

[7] Hendriks CA, Worrell E, de Jager D, Blok K, Riemer P. Emission Reduction of Greenhouse Gases from the Cement Industry. 4th International Conference on Greenhouse Gas Control Technologies, Interlaken, Switzerland 1998.

[8] IEA Greenhouse Gas R&D Programme. CO_2 Capture in the Cement Industry. 2008;2008/3.

[9] ECRA. ECRA CCS Project - Report about Phase II. Technical Report TR-ECRA-106/2009 2009.

[10] IEA Greenhouse Gas R&D Programme. Improved Oxygen production technologies. 2007;IEA report 2007/14.

[11] Kuramochi T, Ramírez A, Turkenburg W, Faaij A. Comparative assessment of CO_2 capture technologies for carbon-intensive industrial processes. Progress in Energy and Combustion Science 2012;38:87-112.

[12] Dean CC, Dugwell D, Fennell PS. Investigation into potential synergy between power generation, cement manufacture and CO_2 abatement using the calcium looping cycle. Energy and Environmental Science 2011;4:2050-3.

[13] Rodríguez N, Murillo R, Abanades JC. CO_2 capture from cement plants using oxyfired precalcination and/ or calcium looping. Environmental Science and Technology 2012;46:2460-6.

[14] Ozcan DC, Ahn H, Brandani S. Process Integration of a Ca-looping Process with a Cement Plant for Carbon Capture. in preparation.

[15] Romeo LM, Catalina D, Lisbona P, Lara Y, Martínez A. Reduction of greenhouse gas emissions by integration of cement plants, power plants, and CO_2 capture systems. Greenhouse Gases: Science and Technology 2011;1:72-8.

[16] Romano MC, Spinelli M, Campanari S, Consonni S, Cinti G, Marchi M et al. The Calcium looping process for low CO_2 emission cement and power. GHGT-11 conference, Kyoto, Japan November 2012.

[17] Rodriguez N, Murillo R, Alonso M, Martínez I, Grasa G, Abanades JC. Analysis of a process for capturing the CO_2 resulting from the Precalcination of limestone in a cement Plant. Industrial and Engineering Chemistry Research 2011;50:2126-32.

[18] EIPPCB. Best Available Techniques (BAT) Reference Document for Iron and Steel Production. 2012.

[19] Birat J, Maizière-lès-Metz D. Steel sectoral report. Contribution to the UNIDO roadmap on CCS - fifth draft. 2010.

[20] Arasto A, Tsupari E, Kärki J, Pisilä E, Sorsamäki L. Post-combustion capture of CO_2 at an integrated steel mill – Part I: Technical concept analysis. International Journal of Greenhouse Gas Control.

[21] Gazzani M, Romano MC, Manzolini G. Application of sorption enhanced water gas shift for carbon capture in integrated steelworks. GHGT-11 conference, Kyoto, Japan November 2012.

[22] Ultra-Low CO_2 Steelmaking (ULCOS) programme. www.ulcos.org. ;September 2012.

[23] World gasification database. www.gasification.org. ;September 2012.

[24] van Straelen J, Geuzebroek F, Goodchild N, Protopapas G, Mahony L. CO_2 capture for refineries, a practical approach. International Journal of Greenhouse Gas Control 2010;4:316-20.

[25] CONCAWE. The potential for application of CO_2 capture and storage in EU oil refineries. CONCAWE Brussels,October 2011;report no. 7/11.

[26] Meerman JC, Hamborg ES, van Keulen T, Ramírez A, Turkenburg WC, Faaij APC. Techno-economic assessment of CO_2 capture at steam methane reforming facilities using commercially available technology. International Journal of Greenhouse Gas Control 2012;9:160-71.

[27] EIPPCB. Best Available Techniques (BAT) Reference Document for the Refining of mineral oil and gas. Draft 2. 2012.

[28] Johansson D, Rootzén J, Berntsson T, Johnsson F. Assessment of strategies for CO_2 abatement in the European petroleum refining industry. Energy 2012;42:375-86.

[29] DET NORSKE VERITAS. Global Technology Roadmap for CCS in Industry. Sectoral Assessment: Refineries. Report No /DNV Reg No : / 12P5TPP-9, Draft Rev 3 2010.

[30] Miracca I, Ingvar Åsen K, Assink J, Coulter C, Curran L, Lowe C et al. The CO_2 Capture Project (CCP): Results from Phase II (2004-2009). Energy Procedia 2009;1:55-62.

[31] Higginbotham P, White V, Fogash K, Guvelioglu G. Oxygen supply for oxyfuel CO_2 capture. International Journal of Greenhouse Gas Control 2011;5:S194-203.