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# Integration of carbon capture technologies in blast furnace based steel making: A comprehensive and systematic review

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# ABSTRACT

Decarbonization of the iron and steel industry, which accounts for 7–9% of global annual emissions, is a strategic objective to achieve carbon emissions reduction targets in line with climate change policies, while maintaining economic competitiveness. Carbon capture (CC) technologies are of critical importance to achieve these goals. This work presents the first systematic review of the integration of CC technologies in the blast furnace-basic oxygen furnace (BF-BOF) steelmaking route, which is expected to maintain a dominant market share over the coming decades. Integration options for post-combustion, looping cycles, oxy-combustion and pre-combustion are described and compared in terms of energy penalty, carbon emissions abatement potential, cost, technology readiness level, and practical deployment considerations. The review yielded 188 studies from peer-reviewed articles and technical papers. Research is mainly focused on chemical absorption, physical adsorption, and oxyblast furnace technologies, but other carbon capture methods including calcium looping, Sorption Enhanced Water Gas Shift, and membranes appear promising in terms of cost and carbon emission reduction. This article provides an in-depth analysis of the current state of the art and crucial considerations for future decision making in the techno-economic selection and integration of CC technologies. Barriers to overcome for practical implementation are also identified and discussed in this article.

# 1. Introduction

Decarbonisation of energy-intensive industries is a strategic objective in European and National policies to accomplish the ambitious target posed in the European Green Deal (2020): to reach a Europe climate neutral in 2050 [1]. The iron and steel (I&S) industry is one of the major industrial contributors to global  $CO_2$  emissions, and is responsible for 5 % of total global greenhouse gas emissions (GHG) [2], mainly due to the current dependency on coal-based processes [3]. In addition, it is a relevant economic sector embedded in strategic value chains that involve 1.3 % of GDP and 330,000 direct employments in Europe with an expected increase in production [4]. Current policies, together with the significant rise in the price of electricity, natural gas (NG) and  $CO_2$  allowances in the past years, is fostering the interest of the sector in the development of low-emission technologies.

Globally, steel is produced through three main routes (Fig. 1): the blast furnace-basic oxygen furnace route (BF-BOF), the scrap-based electric arc furnace (EAF), and the direct reduced iron-electric arc furnace (DRI-EAF). The BF-BOF route consumes mainly iron ore, coal and coke, to cover the 70 % of the global steel demand [2]. Iron ore and coal are processed on a sinter strand and a coke oven, respectively. Then, the hot metal (HM) formed in the blast furnace is send to the basic oxygen furnace to reduce the carbon content and form molten steel.

The scrap-based EAF route uses recycled steel scrap and electricity, encompassing 23 % of the global production, but the expansion of this technology depends on the scrap availability [2]. This process consists only of one stage, the EAF, where the scrap is melted to form new steel. The emerging DRI-EAF route, accounting for 7 % production share [2], includes a shaft furnace, where iron ore is directly reduced by using

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Nomenc	lature	IEA	International Energy Agency
		NGCC PF	P Natural Gas Combined Cycle Power Plant
Abbreviat	ionMeaning	OBF	Oxygen Blast Furnace
BF-BOF	Blast Furnace-Basic Oxygen Furnace	Oxy-TGR	Oxy-Top Gas Recycling
BFG	Blast Furnace Gas	OtherL	Other Looping Processes
BOFG	Basic Oxygen Furnace Gas	Pre-adsor	r Pre-combustion CC with physical adsorption
CC	Carbon Capture	Post-chei	n Post-combustion CC with chemical absorption
CCUS	Carbon Capture Utilization and Storage	Pre-chem	Pre-combustion CC with chemical absorption
CaL	Calcium Looping	Post-men	nb Post-combustion CC with membranes
ChL	Chemical Looping	Pre-mem	b Pre-combustion CC with membranes
COG	Coke Oven Gas	SPECCA	Specific Primary Energy Consumption for CO <sub>2</sub> Avoided
DRI-EAF	Direct Reduced Iron-Electric Arc Furnace	SEWGS	Sorption Enhanced Water Gas Shift
EUA	European Union Allowance	TRL	Technology Readiness Level
FSCM	Fixed Site Carrier Membrane	TGR	Top Gas Recycling
GWP	Global Warming Potential	TSA	Temperature Swing Adsorption
HM	Hot Metal	VPSA	Vacuum Pressure Swing Adsorption
I&S	Iron and Steel	WGS	Water Gas Shift



Fig. 1. The main routes of steel production. . Adapted from [7]

reducing gases such as natural gas, coal syngas, or hydrogen. The resulting direct reduced iron (DRI) is melted, together with scrap, in an EAF. MIDREX [5] and ENERGIRON [6] are commercial-scale processes for DRI production.

Specific energy consumption and CO<sub>2</sub> emissions are very different for each route, and contrasted in Table 1. The BF-BOF process is clearly the most energy intensive one because of the energy needs associated with iron ore reduction in the blast furnace and with the conditioning of the raw materials, iron ore agglomeration and coking processes. The main energy inputs come from coal, giving rise to very high GHG emissions. Despite its high emissions, the BF-BOF route is still under expansion. In China, the I&S industry has developed rapidly over the past two decades, producing almost half of the current global production. Approximately 90 % of China's steel is produced via BF-BOF route [8]. Since the

#### Table 1

Main steelmaking production routes: BF-BOF, Scrap-EAF and DRI-EAF [2].

Steelmaking production route	BF-BOF	Scrap-EAF	DRI-EAF
Steel world production	70 %	23 %	7 %
Main inputs	Iron ore, coal and coke	Scrap and electricity	Iron ore, NG, coal syngas, H <sub>2</sub> , scrap and electricity.
Energy consumption (GJ/tHM)	13–14	4–6	10
CO <sub>2</sub> emissions (tCO <sub>2</sub> /tHM)	2.0–2.2	0.3–0.5	0.7–1.3

global steel demand cannot be covered through recycled scrap, the BF-BOF route is expected to maintain its dominance in the market, despite its high emissions. Besides, blast furnaces are only phased-out at relining, which typically takes places every 20–35 years, or up to 40 years for newly commissioned plants. Thus, at least 20 % of today's blast furnaces are anticipated to still be in operation by year 2050 [9].

The reduction of greenhouse gas emissions from steel production has been the topic of extensive research worldwide. Several alternative ultra-low-CO<sub>2</sub> steel production technologies are under development to replace existing carbon-based steel manufacturing. The project Carbon2Chem [10] studies possible uses for steel gases, while ULCORED [11], ULCOWIN [11], ULCOLYSIS [11], COREX [12], HIsmelt [13], and FINEX [14] are projects and programmes aiming at the development of new routes for steel production. ULCOS-BF [11] and COURSE50 [15] are the only projects focused on capturing  $CO_2$  in the BF-BOF route through physical adsorption and chemical absorption methods from the BFG.

Carbon capture technologies will be necessary to achieve significant carbon emission reduction in the I&S industry. Because of the much larger steel production and specific emissions of integrated steel mills (BF-BOF route) compared to EAF or DRI-EAF, the integrated mills have been the main focus of capture technology development and cost analysis. Besides the huge carbon volume to be captured, another major drawback to integrate  $CO_2$  capture in steel mills is the number of different point sources (Fig. 2). The largest single point source is the blast furnace, from which 70 % of the emissions can be captured, followed by the power plant and the sinter strand. Apart from these processes, other sources emit smaller  $CO_2$  amounts including the coke oven, the basic oxygen furnace or the casting and rolling. Since the emission rate and the mole fraction of  $CO_2$  are very different among the various sources, multiple carbon capture plants or combining flue streams would be needed for each large mill in order to capture a large proportion of the total emissions. I&S gases, unlike flue gases from power production, have the particularity that besides  $CO_2$  and  $N_2$ , other gas species are present at important concentrations, notably CO,  $H_2$  and  $CH_4$  (Table 2). However, steel gases have a higher  $CO_2$  concentration than flue gases from power production.

Previous reviews related to low carbon ironmaking have not focused on CC or the BF-BOF route [18–21]. The main objective of this article is to present a systematic review of the state of the art related to carbon capture (CC) within the I&S industry, with special focus on the BF-BOF route. A global and holistic picture is presented to assist decision making regarding the most promising CC technology for the BF-BOF steelmaking route, by evaluating and comparing the technologies in terms of energy penalisation, economic cost, efficiency, Technology Readiness Level (TRL) [22], and the volume of  $CO_2$  captured.

The paper is organised as follows: Section 2 presents the methodology of the systematic review; Section 3 comprises the post-combustion carbon capture systems; Section 4 include the looping carbon capture

# Table 2

vpical composition for steel gases 171 and power plant flue gase	ases (%vol).
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	Units	BFG	COG	BOFG	Coal PP	NGCC PP
$H_2$	%vol	4	45–64	1.5	_	-
$CH_4$	%vol	-	20-30	-	-	-
CO	%vol	22-25	5–10	60–70	-	-
$CO_2$	%vol	20-22	2–5	15 - 20	13	4
$O_2$	%vol	-	1–4	2	5	14
$N_2$	%vol	49–54	0–5	10	82	82
LHV	MJ/Nm <sup>3</sup>	3–3.8	16-19.3	7.5-8	-	-



Fig. 2. Simplified flow sheet of an integrated steel mill, showing CO<sub>2</sub> emissions (kg/t steel) and concentration in flue gas (volume %) [16].

# Table 3

Search terms, number of hits returned and number of papers reviewed.

$\mathrm{N}^\circ$	Search term	Hits	Reviewed
0	("Iron plant" OR "Iron industry" OR "Ironworks" OR "Ironmaking" OR "Iron-making" OR "Iron production" OR "Iron refining" OR "Steel plant" OR "Steel industry" OR "Steelworks" OR "Steelmaking" OR "Steel-making" OR "Steel production" OR "Steel refining" OR "Blast furnace" OR "Basic oxygen furnace" OR "Coke Oven" OR "Sinter plant" OR "Sinter strand")	Commo terms fo searche	n I&S or all the CC s
1	("Carbon capture" OR "Carbon dioxide capture" OR "CO2 capture" OR "CC" OR "Carbon utilization" OR "Carbon dioxide utilization" OR "CO2 utilization" OR "Carbon utilisation" OR "Carbon dioxide utilization" OR "CO2 utilisation" OR "CCU" OR "CCUS" OR "Carbon recycling" OR "Carbon dioxide recycling" OR "CO2 recycling" OR "Carbon dioxide recycling" OR "CO2 reduction" OR "CCU" OR "Carbon dioxide reduction" OR "CO2 reduction" OR "Carbon dioxide reduction" OR "CO2 reduction" OR "CO2 mitigation" OR "Carbon dioxide mitigation" OR "CO2 mitigation" OR "Low carbon" OR "Decarbonization" OR "Decarbonisation" OR "Emission reduction" OR	971	35
2	("Amine gas treating" OR "Amine scrubbing" OR "Amines" OR "MEA" OR "DEA" OR "MDEA")	92	15
3	("Oxy combustion" OR "Oxycombustion" OR "Oxy- combustion" OR "Oxyfuel" OR "Oxy-fuel" OR "Oxy-fuel combustion")	44	3
4	("Top gas recycling" OR "TGR" OR "Top gas injection" OR "BFG injection" OR "Hot Reducing Gases" OR "HRG")	118	37
5	("Precombustion capture" OR "Pre-combustion capture" OR "Pre combustion capture" OR "CO2/H2 separation" OR "Partial oxidation")	130	2
6	("Membranes" OR "Membrane separation" OR "Membrane-based separation" OR "Membrane technology")	84	7
6	("Calcium looping" OR "Calcium-looping" OR "Ca- Looping" OR "CaL" OR "Carbonate looping" OR "Chemical looping" OR "Chemical-looping" OR "Combustion looping" OR "Oxygen carrier")	68	15
8	("Pressure Swing Adsorption" OR "PSA" OR "Temperature Swing Adsorption" OR "TSA" OR "Vacuum Swing Adsorption" OR "VSA" OR "VPSA" OR "DTSA")	62	6
	Total	1569	120

systems; Section 5 contain the oxygen blast furnaces and top gas recycling technologies; Section 6 comprises pre-combustion carbon capture systems; and Section 7 presents a carbon capture technologies comparison.

# 2. Systematic review approach

To identify the most relevant literature on the topic, a systematic review approach was adopted. Web of Science was selected as the search engine because of its advanced search capabilities and wide range of databases. The search is limited to studies presented in scientific journals and conferences included in the selected search engine. A set of 7 searches were performed, returning a total of 1569 entries (Table 3). Each search combined a term related to the I&S process (N° 0) and another term concerning carbon capture and storage (N° 1 to 7). The hits returned from the search were screened based on their abstract, and selected for review when applying any type of CC on the BF-BOF route of the I&S industry, leading to a total of 120 articles.

The 120 research articles were reviewed and classified into four different topics, according to the typical CC technology classification: post-combustion, looping cycles, oxy-combustion, and pre-combustion [23]. Fig. 3 illustrates the different options available for each CC technology. Each type of technology, if applicable, is divided according to the specific CC technology applied within the category: chemical absorption, physical adsorption, membranes, calcium looping, chemical looping and sorption enhanced water gas shift (SEWGS). For example,

for oxy-combustion CC technology, only oxygen blast furnace technology was found (i.e., oxy-combustion CC technology of BOFG or other gases were not found in the literature).

Articles purely related to the improvement of energy efficiency, fuel consumption reduction,  $H_2$  production without carbon capture, injection of hot reducing agents in the BF without carbon capture, steam methane reforming, and carbon dioxide reforming of methane were not included in this review since  $CO_2$  is not captured or used directly. Articles related to CC in other steelmaking routes (i.e., DRI or EAF) were also not considered.

## 3. Post-combustion CC in BF-BOF

Post-combustion technologies include those systems where  $CO_2$  is captured from the flue gases. This section reviews chemical absorption and membrane separation techniques for carbon capture in the I&S industry, and is focused on those previous works related to decarbonization of gas streams with no presence of combustible gases or including a stage of water-gas shift reactor to convert CO into  $CO_2$ . Research works, where the resulting cleaned gas is considered as a useful fuel, are classified in Section 6 as pre-combustion capture.

## 3.1. Post-combustion $CO_2$ capture by chemical absorption

Chemical absorption systems are based on chemical solvents that react reversibly with a certain target species. This method allows for a very selective separation compared to other technologies, and high purities and recoveries. Difficulties arise from the handling of the solvent systems, often exhibiting corrosive or volatile characteristics, as well as from the regeneration process of the saturated absorbent, usually endothermic, necessary for the economical operation of the separation.

The typical operation of industrial absorption consists of two stages: absorber to capture the CO<sub>2</sub> from the acid gas, and stripper to release the captured CO<sub>2</sub>, as shown in Fig. 4. In the latter, the rich solution (amine + CO<sub>2</sub>) is heated up to 110 °C in order to recover the CO<sub>2</sub> in a concentrated gas stream. The lean solution exiting the stripper is recycled back to the absorber. The global efficiency is increased by including a heat exchanger, where the rich solution is pre-heated before entering the stripper using the outgoing lean solution.

# 3.1.1. Solvents and associated energy penalizations

In the context of the I&S industry, chemical absorption has been investigated for carbon capture from the flue gases of BF hot stoves [24–28], power plants [29–32], and coke ovens [24,33]. Concurrent carbon capture from different sources has been also studied in other works, aiming for a bigger  $CO_2$  emission reduction [34,35,44,36–43].

The most widely used chemical solvents are single-component alkanolamines in an aqueous solution. These are classified into three categories depending on the type of the amine functional group: primary such as monoethanolamine (MEA) and diglycolamine (DGA), secondary such as diethanolamine (DEA), isopropylaminoethanol (IPAE) and aminoethylethanolamine (AEEA), and tertiary such as piperazine (PZ) and methyldiethanolamine (MDEA). They exhibit different behaviour with regards to reaction rates, heats of reaction, and corrosion. Primary amines are the most reactive, possess the highest heat of reaction, and are usually the most corrosive. These properties are less pronounced for secondary and tertiary amines. In addition to single-component amines, some multi-component solvents (RITE-A and RITE-B) have been developed by the Research Institute of Innovative Technology for the Earth (RITE) [28]. These novel solvents are IPAE-based mixtures of amines.

The most commonly used amine solvent is monoethanolamine (MEA), while other solvents have barely been studied in the literature (see Table 8). The high heat of reaction results in energy penalties ranging from 2.9 MJ/kgCO<sub>2</sub> to 6.5 MJ/kgCO<sub>2</sub> for MEA (30 %wt MEA) [24,25,34,36–38,40,42,43,45,26–33] and between 2.9 MJ/kgCO<sub>2</sub> and 3.1 MJ/kgCO<sub>2</sub>, for MDEA (50 %wt MDEA) [35,39]. Yang et. al. [44]



Fig. 3. Carbon capture routes in the Iron and Steel industry (BF-BOF route).



Fig. 4. CO<sub>2</sub> capture with chemical absorption.

investigated a mixture of 40 % MDEA with 10 % PZ obtaining a thermal consumption of 2.3 MJ/kgCO<sub>2</sub>. For the solvents RITE-A and RITE-B, the standard thermal penalizations are 3.3 MJ/kgCO<sub>2</sub> and 3.1 MJ/kgCO<sub>2</sub>, respectively, but after optimization for RITE-B, 2.5 MJ/kgCO<sub>2</sub> can be achieved. [28]. Cheng et. al. [25] compared the heat of reaction for MEA, AEEA, PZ, and their mixtures with respect to CO<sub>2</sub> capture in the

hot stove flue gas. The study showed 10 % less consumption for PZ than for MEA and AEEA, which exhibit similar thermal penalization (3.7 MJ/  $kgCO_2$ ).

Among these articles, only a few works [26,30,37,38,42-44] studied the electricity consumption of carbon capture, ranging from 0.28 to 1.5 MJ/kgCO<sub>2</sub>. This electricity consumption is related to the required CO<sub>2</sub>

# Table 4

Main KPIs for pre-combustion CC with membranes in the I&S industry.

Source	Baker (20	)18) [59]	Luca (2021) [41]	Yun (20	)21) [42]								
Membrane Permeab. (gpu) Selectivity CO <sub>2</sub> /N <sub>2</sub>	Polaris 1500 25		PVAm 371 200	Polyimi 500 20	ide								
Membrane configuration	Two- stage A	Two-stage B	Two- series	Two-sta	age B					Two-st	age A		
CO <sub>2</sub> Source	BF stoves	BF stoves	BOFG	BF stov	es	Utility	PP	Lime		Coke		Sintering	5
Inlet %CO <sub>2</sub>	25,0	28,0	21,1	27,3		26,4		19,4		14,8		4,8	
Purification and compression	Cond + rec	Mem + Cond +	-	-	Cond + Mem +	-	Cond + Mem +	-	Cond + Mem +	-	Cond + Mem +	-	Cond + Mem + rec
Pressure of CO <sub>2</sub> stream (bar)	150	150	120	1–2	152	1–2	152	1–2	152	1–2	152	1–2	152
Spec. Consump. (kWh <sub>e</sub> /tCO <sub>2</sub> )	286	235	327	207	318	235	320	302	393	330	473	1063	1220
Spec. Consump. (MJ/kgCO <sub>2</sub> )	1,03	0,846	1,18	0,745	1,15	0,846	1,15	1,09	1,42	1,19	1,7	3,83	4,39
Membrane area (m <sup>2</sup> /(tCO <sub>2</sub> /h))	3400	2780	5114	2543	1953	3079	2659	4080	4515	4724	5504	37,894	13,321
CO2 inlet (tCO2/h)	41,7	220	6,8	189	189	448	448	32,7	32,7	87,4	87,4	15,3	15,2
Captured CO <sub>2</sub> (tCO <sub>2</sub> /h)	33,3	176	6,4	171	170	404	404	29,5	29,5	78,4	78,4	13,7	13,7
Capture rate of CO <sub>2</sub> (%)	80	80	94	90	90	90	90	90,1	90,1	89,7	89,7	89,7	90
CO <sub>2</sub> purity in outlet stream (%)	99	99	95,5	90									
CapEx (\$/(kgCO <sub>2</sub> / h)	1482	1248		1325	1651	1537	1709	2119	2932	2319	3094	9190	8912
Cost of electricity (cS/kWh <sub>e</sub> )	5	5		6									
Manthe (y)	0	0	-	50									
Niembrane life (y)	3	3	5	5									
Capacity factor (%)	47	0.0	93	85	50 5	14.4	- 4	( <b>1</b> =			01.0	071 7	050 5
(\$/tCO <sub>2</sub> )	47	<i>3</i> 6		41,7	52,5	46,6	54	64,7	83,3	70,7	91,2	2/1,/	252,7

compression work for transport and storage. Both consumptions, thermal and electrical, give an overall equivalent electricity penalization between 1.1 MJ/kgCO<sub>2</sub> and 3.8 MJ/kgCO<sub>2</sub> for this specific technology.

### 3.1.2. CO<sub>2</sub> emission reduction, technology readiness level and costs

The CO<sub>2</sub> capture process by amine solvents is mature (TRL 9) and already commercialized in natural gas or fertilizers processing plants [46]. Nevertheless, no large-scale project has been found in the literature regarding post-combustion capture with chemical absorption in the I&S industry. This could be due to the large CO<sub>2</sub> amounts, the high costs, and the geological storage difficulties. Most of the published works are theoretical studies. The reported emission reductions range between 11 % and 77 %, corresponding to 230 kgCO<sub>2</sub>/tHM and 1700 kgCO<sub>2</sub>/tHM, respectively [24,26,36–45,27,29–35].

Only two experimental studies were identified. Cheng et al. [25] investigated the  $CO_2$  capture in a rotating packed bed from a hot stove flue gas flow of 33 l/min containing 30 vol%  $CO_2$ . The research was focused on thermal energy consumption with different solvents (MEA, AEEA, PZ and their mixtures), but the  $CO_2$  emission reduction was not assessed. The alkanolamine solutions with 10 %wt PZ and 20 %wt MEA or AEEA were found to be the most effective absorbents to capture  $CO_2$ . Goto et al. [28] presented a pilot plant of 1 tCO<sub>2</sub>/day installed at the Kimitsu works of Nippon Steel Co. The CC plant was fed with the blast furnace flue gas and tested with MEA, RITE-A, and RITE-B. RITE solvents were developed with IPAE, and the best regeneration energy calculated was 2.5 MJ/kgCO<sub>2</sub> for an ideal operation with RITE-B.

Since post-combustion carbon capture does not offer any

technological or economical advantage (such as increased energy efficiency or fuel-saving), it will always result in a financial burden. The key factor for the installation of a carbon capture stage is the CO<sub>2</sub> tax price. If this price is higher than the carbon capture cost, capturing the CO<sub>2</sub> will be profitable as compared to emitting it into the atmosphere. Until 2018, the European Union Allowance (EUA) price was always below 16 \$/tCO<sub>2</sub>, but since then, it has increased to reach 91 \$/tCO<sub>2</sub> in February 2022 [47]. According to the literature, capture costs are between 38.2 \$/tCO<sub>2</sub> and 204 \$/tCO<sub>2</sub> for MEA solvent (with an average of 77.4 \$/tCO<sub>2</sub>) [24,26,32,36–38,40,42,43], 76–81 \$/tCO<sub>2</sub> for MDEA [35,39], and about 97 \$/tCO<sub>2</sub> for a mixture of MDEA and PZ [44]. Therefore, based on the current scenario of EUA prices, establishing a carbon capture stage is profitable in most cases.

#### 3.2. Post-combustion CO<sub>2</sub> capture with membranes

Membrane is a cost-effective emerging technology for carbon capture in power plants and energy intensive industries. Gas separation with membranes takes advantage from the different permeation rates of certain materials to specific species, when both sides of the membrane are subjected to a differential pressure. The few theoretical works published in the literature related to I&S industry (TRL-2) are reviewed in this section.

#### 3.2.1. Materials and characterization of membranes

Different materials including polymers [48], inorganic compounds [49,50], metal-organic frameworks [51], zeolite imidazolate





Fig. 5. Configuration of two-stage membrane-based  $\mathrm{CO}_2$  capture. . Adapted from [42]

frameworks [52,53], graphene oxide [54], and micro porous hollow fibers [55] have been investigated for CO<sub>2</sub> separation. Membrane performance is mainly assessed through the properties of selectivity and permeability, which traditionally have involved a trade-off among them. The gas permeance is the permeated flow per membrane area and per differential pressure across the membrane (gas permeance unit: 1gpu = $2.7 \cdot 10^{-3}m^3(STP)/(m^2 \cdot h \cdot bar)$ ). Permeability is the product of permeance and membrane thickness, while the selectivity is the ratio of permeability coefficients of two gases defined greater than unity [56]. Other important characteristics to be considered are stability, mechanical resistance, and easy and cost-effective manufacturing.

Gas transport mechanism mainly consists of three steps: dissolution, diffusion, and desorption of permeate (solution-diffusion transfer mechanism). Additionally, the presence of reactive carriers in the membrane may enhance mass transfer and selectivity (facilitated transfer mechanism). Accordingly, selectivity and permeability of a membrane to a certain gas depend on the relative size of molecules with respect to pore size and on the difference in the solubility, diffusivity and/or reactivity with certain mass carriers as compared to that of other species present in the gas stream. Solubility selectivity favors small molecules [48]. Higher permeability results in lower differential pressure and membrane area, and therefore lower costs, while higher selectivity produces higher purity in the permeate, but higher costs.

Commercially available membranes already exist for the separation of H<sub>2</sub> and CO<sub>2</sub> [57], i.e. Polaris<sup>TM</sup> (MTR, Inc.), the first commercial membrane developed specifically for post-combustion. Nevertheless, this capture technology is currently under development stage (TRL-6), with only one small pilot plant operating in Norcem Cement at Brevik (Norway), where 70 mol% CO<sub>2</sub> purity was achieved with a single membrane stage [58]. Current developments are mainly focused on power plants because of the global volume of the involved emissions [59]. However, since the costs of CC strongly decrease with CO<sub>2</sub> concentration in the inlet flow, steel and cement plant gases (20–30 vol%) are favored with respect to power plant gases (12–15 vol%) [59]. In the presence of CO, it is desirable to include a stage of water-gas shift reactor to increase CO<sub>2</sub> concentration. Additionally, since membranes are easily poisoned by sulphur components, a previous desulphurization stage is required to lower the SO<sub>2</sub> concentration to levels of 10–25 ppmv [57].

#### 3.2.2. Configurations and KPIs

There is no experimental study published in the literature related to the integration of membrane-based  $CO_2$  capture systems in the I&S industry. Only a few theoretical research works can be found. Membranes operation is based on a sufficient partial pressure difference between the feed and the permeate stream sides. Since the BFG is at  $\sim$ 3 bar, there are two options: (i) to pressurize the BFG before entering the separation system [57], or (ii) to install a vacuum pump on permeate-side [59]. The latter option is preferred as it consumes less energy.

Given that the optimal range for a low-cost capture based on membranes is that where the rate of  $CO_2$  capture is from 50 to 70 % in the first step [59], at least two membrane stages are needed for higher capture rates. Different configurations have been simulated for the principal  $CO_2$  emission sources in I&S industry. The main results found in the literature are summarized in Table 4. Luca & Petrescu [41] investigated a  $CO_2$  capture system with two spiral wound membranes connected in series with recirculation of 30 % and 5 % of permeate and pressure ratios of 100 and 80 for the first and second stage, respectively. The flue gas stream contained 21.1 vol%  $CO_2$ , while the output  $CO_2$  stream reached a purity of 95.5 %. The capture rate was 94 % with a specific energy consumption of 327 kWh/tCO<sub>2</sub>.

The two-stage concepts of Fig. 5 have been also explored in [42,59]. Retentate or permeate after the second membrane is recycled in configurations A and B, respectively. The former is more suitable for 20–25 vol% CO<sub>2</sub>, while streams containing more than 25 % are better treated by the latter. Baker et al. [59] used Polaris<sup>TM</sup> membrane [60] in both cases including a CO<sub>2</sub> condensation column for purification (>99 %, 30 bar, -25 °C) and the subsequent compression up to 150 bar. Configuration A was applied to a stream of 1000 t<sub>CO2</sub>/day with a typical composition of cement industry (25 vol% CO<sub>2</sub>), which is similar to that of the flue gas of BF stove or of utility power plant in I&S industry. The first stage increases CO<sub>2</sub> concentration up to 40 vol%, capturing about 60 % of incoming CO<sub>2</sub>. The second stage enriches permeate gas above 75 vol%, reaching a global capture rate of 80 %. The electric



Fig. 6. Configuration of a Calcium Looping-based CO2 capture process.

consumption is 286 kWh/tCO<sub>2</sub>, the required membrane area is 3400 m<sup>2</sup>/ (t<sub>CO2</sub>/h) and the total cost of capture is 47 \$/tCO<sub>2</sub>. Configuration B was applied to a typical composition of BF stoves flue gas [61] with 28.5 vol % CO<sub>2</sub>. The first and second membranes reduce CO<sub>2</sub> concentration from 28 % to 17 % and 8 %, respectively, representing a global capture of 80 % of incoming CO<sub>2</sub>. The resulting permeate stream is further enriched (above 80 %) through a third membrane module before the condensation column. The electric consumption is 235 kWh/tCO<sub>2</sub> and a membrane interface of 2780 m<sup>2</sup>/(t<sub>CO2</sub>/h) is required. The total cost of capture is 36 \$/tCO<sub>2</sub>.

Yun et al. [42] used a polyimide membrane in both the configurations of Fig. 5, analyzing separately the effect of purification (dehydration and stripping column) and final compression up to 152.7 bar. For the sake of comparison, the capture rate and the mole fraction of  $CO_2$ were set to 90 %. Configuration A was applied to sinter strand (4.81 vol %) and coke oven (14.77 vol%) gases, while configuration B was implemented for flue gases of lime production (19.41 vol%), power plant (26.43 vol%) and BF stoves (27.3 vol%). Electricity consumption and the required membrane surface area sharply increase below 10 vol%  $CO_2$  in the inlet stream. Carbon capture costs increase with lower  $CO_2$ incoming content from 42 \$/tCO<sub>2</sub> in the latter case (BF stoves) to 272 \$/tCO<sub>2</sub> in the former case (sintering process).

According to these theoretical results, membrane-based capture systems could be a competitive solution for  $CO_2$  rich streams. Nevertheless, further experimental research is required for such systems to become available at commercial scale.

## 4. Looping processes for CC in BF-BOF

Carbon capture with looping processes include those systems where CO<sub>2</sub> is captured either in combustible gases or in flue gases. This section review calcium looping (CaL), chemical looping (ChL) and other looping processes (OtherL), including Ca-Fe or Ca-Cu for carbon capture in the I&S industry.

#### 4.1. Calcium looping

Calcium looping (CaL) is a CC technology where calcium oxide (CaO) is reacted with  $CO_2$  to form calcium carbonate (CaCO<sub>3</sub>), and CaCO<sub>3</sub> is then heated to regenerate CaO and CO<sub>2</sub> in a calciner (see Fig. 6). The calcination process in endothermic, and a fuel input to the process is required. The captured  $CO_2$  can then be used or transported for storage. The few theoretical works published in the literature related to I&S industry (TRL 2–3) are revised in this section.

Cormos performed a technoeconomic evaluation of a Calcium Looping (CaL) carbon capture process in post-combustion as the alternative to decarbonise an integrated steel mill [35]. A conventional integrated steel mill (4 million tonnes Hot Rolled Coil per year output) with CaL carbon capture was analysed under two scenarios which accounted for the most important CO<sub>2</sub> emission sources within the steel mill (e.g., power plant, hot stoves, lime plant, coke ovens). The carbon capture efficiency, specific CO<sub>2</sub> emissions, and CO<sub>2</sub> capture investment costs of the integrated steel mill with CaL capture process were evaluated (see Table 8). The evaluated captive power plants and the carbon

capture process were thermally integrated using pinch method. Heat integration is of importance considering the multiple heat sources within the steel plant to be used to cover the energy duties. Heat integration is especially critical for CaL processes to quantify the high temperature heat recovery potential. Chisalita et al. explored the environmental aspects of this configuration through a Life Cycle Assessment using the functional unit of 1 tHRC [34]. Global warming potential (GWP) of the integrated steel mill was reduced by 64-75 % when CaL was coupled (emitting 516–754 kg CO<sub>2</sub> eq/tHRC). The GWP even shows negative values given the negative CO2 emissions allocated to the exported electricity. Nevertheless all other environmental indicators (acidification potential or eutrophication potential) have a more or less significant increase compared to the benchmark case, associated to the extraction and transportation of the natural gas required in the calciner (71.8-119 kg of natural gas/tHRC). The economic penalty of CaL capture leads to a 6 % increase of specific capital investment and a 12 % increase of steel production cost [39].

CaL capture process can be also applied in precombustion for the production of hydrogen from raw coke oven gas (COG) by means of  $CO_2$  sorption enhanced steam reforming using CaO as  $CO_2$  sorbent (CaL-SESR). Xie et al. thermodynamically analysed this process, and estimated equilibrium compositions, energy consumption, and  $CO_2$  emissions [62]. This configuration can lead to concentrations over 95 vol% H<sub>2</sub> in the reforming gas while reducing the temperature of the reforming processes, the  $CO_2$  emission, and the total energy demand per unit of generated hydrogen in comparison to conventional reforming. The CaL-SESR process avoids 99 % of  $CO_2$  generated from the COG after a conventional reforming.

Halmann and Steinfeld also studied the enhanced reforming of blast furnace gas (CO<sub>2</sub>, CO, N<sub>2</sub> and H<sub>2</sub>) through CaL capture process from a thermodynamic modelling approach. Partial or complete carbon capture can be achieved depending on the operating conditions of the SESR reactor and a relatively pure CO<sub>2</sub> produced. The implications of such reactions with respect to hydrogen production, CO<sub>2</sub> emission avoidance and process efficiency are presented in this work [63].

Liu et al. experimentally explored the sorption enhanced water gas shift (SEWGS) reaction to improve the carbon capture from BFG. The CO in the BFG was first converted to CO2 and, then, captured through carbonation reaction. The lab-scale experimental results from this study highlighted the importance of the sorbent type on the SEWGS reaction, with both CaO and MgO in the sorbent catalyzing the reaction. WGS reaction becomes the rate limiting step for calcined limestone, while for calcined dolomite, WGS reaction is not a limiting step and most of the CO2 for the CaO carbonation comes from WGS reaction on MgO surface. Besides, it was observed that not only CaO but also MgO experienced the decay in the catalytic reactivity after multiple cycles [64]. Tian et al. deepen the study of this concept combining CaL CO<sub>2</sub> capture and waste recycling into I&S production. The sorbents used in this experimental study were CaO-based, 90 wt% CaO, obtained from steel slag which showed better reactivity and slower deactivation than commercial CaO. The preparation of steel slag as sorbents co-produces high-quality iron ore with iron content of 55.1-70.6 % which compensate the larger costs when compared to naturally derived CaO. The cost of the steel slagderived CO<sub>2</sub> sorbent achieves 57.7  $\ell$ /t, which makes this material a cost-effective option for CO<sub>2</sub> removal in I&S industry. [65].

Tian et al. also performed a techno-economic study of this CaL decarbonisation concept for steelmaking showing a substantial and cost-effective CO<sub>2</sub> emission reduction and the superiority of CaL in comparison to other technologies [66]. The cost of avoided tonne of CO<sub>2</sub> is reduced down to 12.5–15.8  $\epsilon$ /tCO<sub>2</sub> (below one third the cost obtained using amine scrubbing technology) while the emissions can be reduced up to an 80 %.

Calcium looping technology has a demonstrated TRL 6, achieved through experimental experimentation with fluidized bed reactors at significant scale and relevant operating conditions for industrial applications [67–69]. Over fourteen CaL experimental plants of different



Fig. 7. Configuration of a Chemical Looping-based CO<sub>2</sub> capture process.

sizes from few kWth to MWth have been constructed and operated worldwide [70] while its feasibility at 1–2 MWth scale has been demonstrated through the operation of two large pilot plants [71–73]. The concept itself has been completely demonstrated and its applications to industry has been explored at lower TRLs through the integration with power and cement plants [69,70]. Several ongoing projects target to demonstrate the technical feasibility of industrial integration of CaL capture processes at large scale in relevant environments. CLEANKER project aims at demonstrating at TRL 7 the CaL concept with 90 % of CO<sub>2</sub> capture in a fully integrated configuration with a cement production process. Instead of fluidized beds, this project proposes the use of entrained flow reactors which are well-known equipment in the cement industry [74]. C4U project also targets to elevate two modified CaL carbon capture processes, DISPLACE and CASOH, from TRL 5 to 7 and to design for optimal integration in the steel industry [75].

# 4.2. Chemical looping

The Chemical Looping (ChL) concept is based on the transfer of oxygen from air to the fuel by means of a metal oxygen carrier, avoiding direct contact between fuel and air (see Fig. 7).Fig. 8.

The utilisation of chemical looping (ChL) as an option of CO<sub>2</sub> capture in the I&S industry has focused on the development of alternatives for the combustion coke oven gases (COG) without CO<sub>2</sub> emissions, or H<sub>2</sub> production for the steel process or other uses such as NH<sub>3</sub> production.

In the case of power production with steel gases, a chemical looping combustion (CLC) combined cycle using COG as fuel was proposed in [76]. Low TRL levels (2–3) are reached as the technology concept has been just formulated using ASPEN simulation considering Ni-based oxygen carriers NiO/NiAl<sub>2</sub>O<sub>4</sub> (60:40 wt%) due to good results for CO<sub>2</sub> capture applications [76]. Nevertheless, others oxygen carriers composed of Fe<sub>2</sub>O<sub>3</sub>/CuO and MgAl2O4 have been investigated using

thermogravimetric analysis (TGA) and a laboratory pressurised circulating fluidised bed system for this specific applications in a 3–10 kWth test rig [77].

H<sub>2</sub> production based on CLC has been also suggested for decarbonising I&S production. For Chemical-looping water-splitting (CLWS), an additional reactor is required in a three-stage process that combines the concepts of CLC and steam-iron process [7879]. In this new stage, compared with CLC, steam reactor, the oxygen carrier is partially oxidised by steam to yield H<sub>2</sub> that provides a decarbonised fuel source for producing direct reduced iron (DRI) [78]. Low TRL are also suggested (2/3), with the concept formulated and some integration schemes analysed to improve state-of-the-art options by reducing the amount of coke used in the sintering plant, increasing thermal energy efficiency, CO<sub>2</sub> capture ratio [80] and exergy efficiency [79]. Moreover, some researchers have also proposed to use H<sub>2</sub> generated to produce ammonia, integrating this scheme with pressure swing adsorption technology [81]. In all these alternatives, 100 % direct CO<sub>2</sub> capture efficiency and improved economic figures, compared to the present technologies, could be achieved.

Regarding CLC, there is a general consensus that the maturity of the technology has reached a TRL of approximately 6 [46,82–84]. At least 46 CLC pilot rectors have been successfully constructed and operated with gaseous, liquid, and solid fuels [85,86]. Although the CLC concept and its performance has been completely demonstrated, its applications to industry remain unexplored. Fortunately, recent planned research projects have been proposed to fill this gap. CHEERS project is going to develop a CLC system, with inherent carbon capture, to increase CLC TRL to 7 [87]. The system is designed for deployment in a refinery environment, with petroleum coke as fuel, and to produce high temperature steam. It will have a thermal power of 3 MW and will combine oxygen polisher, a heat recovery steam generator, CO<sub>2</sub> capture, as well as compression and purification of the CO<sub>2</sub> in compliance with



Fig. 8. Configuration of a Ca-Cu based  $\mathrm{CO}_2$  capture process, . adapted from [90,91]



Fig. 9. Process flow diagrams of oxygen blast furnaces with top gas recycling, compared to an air-blown blast furnace.

specifications for enhanced oil recovery [88]. Also, LOUISE project [89] aims to demonstrate CLC of solid refuse fuels using ilmenite as the oxygen carrier at a TRL 6 (150 kWth and 1 MWth) and to accelerate the deployment of CLC by providing the basic design of a 10 MWth CLC demonstration plant (TRL 7) for waste-derived fuels. There are no specific projects or applications of CLC for the steel sector, but the challenges that ongoing projects have to face would be similar to those of CLC in the steel sector.

# 4.3. Other looping processes

The combination of calcium Looping (CaL) and chemical looping combustion (CLC) has also been proposed for the blast furnace gas (BFG) utilisation. There are two main routes for this process depending on the metal that is combined with calcium: Ca-Fe or Ca-Cu. Both alternatives are promising and have similar level of development (TRL 2/3).

Combined CaL processes have been investigated by Tian et al., who developed a new material to be used in a combined Ca-Fe chemical loop using steel slag as feedstock. In the case of iron, using steel slag as feedstock, the CaO-based, Fe-functionalized CO<sub>2</sub> sorbent (Fe<sub>2</sub>O<sub>3</sub> and CaO) have shown promising potential with stable cyclic CO<sub>2</sub> uptaking 10 realistic combined Ca–Fe looping cycles [92]. This is also a three-stage process, where the heat released due to FeO oxidation provides the heat to drive the endothermic CaCO<sub>3</sub> decomposition reaction.

For the copper alternative, there are two schemes proposed. The first one, based on packed-bed, converts mainly blast furnace gas (BFG) into H<sub>2</sub>/N<sub>2</sub> together with the release of a large amount of high temperature heat [8]. Around 30 % of the BFG can be upgraded via calcium loopingassisted water gas shift (WGS). Decarbonised fuel gas could be used for onsite power generation or to obtain sponge iron by a Direct Reduced Iron (DRI) process, thus increasing the overall capacity of the steel plant and avoiding the CO<sub>2</sub> emissions. Low values for the specific energy consumption of around 1.5 MJLHV/kgCO<sub>2</sub> and CO<sub>2</sub> capture efficiencies higher than 95 % support the further development of the proposed Ca-Cu looping [91]. The second scheme uses a sorption enhanced water gas shift (SEWGS) reactor with blast furnace gas (BFG) of steel mills. CO<sub>2</sub> is simultaneously removed from the gas using a CaO based sorbent. A Cu/CuO chemical loop supplies the energy required for the regeneration of the sorbent via the exothermic reduction of CuO with coke oven gas (COG) [93]. Approximately 27 % of the BFG can be decarbonised in the SEWGS reactor while also producing H<sub>2</sub>. A CO<sub>2</sub> capture ratio of 31 % (CO<sub>2</sub> capture efficiencies of up to 95 %) with respect to the total carbon emissions in the steel mill can be achieved. More than 60 % of the thermal input can be recovered as high-temperature heat, which could be efficiently recovered for producing electricity [93]. This represents a clear improvement when compared with a steelmaking plant with a post-combustion MEA absorption system [31] and allows the utilisation of the excess of H2-rich gas in the Ca-Cu steel plant to produce additional iron through a direct reduction iron (DRI) process. It has been demonstrated that the production capacity of the steel plant can be increased by around 10.5 % without installing a purpose-built and high-cost NG reforming plant [31,90].

Sun et al. proposed a system for coupled decarbonisation and

desulfurization of BFG via a magnesium-molybdenum looping process [94]. The system includes a desulfurization-decarbonization reactor and a regenerator. Four carbon-sulfur carriers were screened, highlighting MgO-MoO<sub>3</sub> as the most capable sorbent for decarbonisation and desulfurization. Results showed that temperatures over 240  $^{\circ}$ C decrease in carbon capture efficiency. Carbon removal efficiency reached values up to 99.70 % and complete sulfur removal.

# 5. Oxygen blast furnaces and top gas recycling for CC in BF-BOF

The most spread strategies for carbon mitigation in the I&S industry are the oxy-fuel combustion in the oxygen blast furnace (OBF) and the top gas recycling (TGR). The former uses O<sub>2</sub>-enriched air as hot blast for the combustion of coke and the auxiliary fuels, producing a top gas with very little content of nitrogen [95], while the latter recirculates part of the top gas to the blast furnace, usually after a carbon capture stage. Both strategies are usually combined to make use of the synergies among them.

#### 5.1. Type of configurations and associated penalties

The difference between oxy-fuel systems for power production, and oxygen blast furnaces, is that the former performs complete combustion (i.e., exhaust gas mainly composed by  $CO_2$  and  $H_2O$ ) [96]. In oxygen blast furnaces there is incomplete combustion to obtain CO and  $H_2$ , which are then used to reduce the iron oxides (i.e., top gas composed mainly of CO,  $CO_2$ ,  $H_2$ , and  $H_2O$ ) [97].

Conventionally, in oxy-fuel combustion, a part of the exhaust gas is recirculated to palliate the lack of nitrogen and its sensible heat, aiming for keeping similar fluid- and thermo-dynamic behavior than in airblown combustion [98,99]. However, injecting CO<sub>2</sub> or H<sub>2</sub>O to the blast furnace is not desirable as it increases the coke consumption and hinders the reduction of iron oxides because of displacing the chemical equilibrium. Therefore, a carbon capture stage is usually included before recycling the top gas, in order to reject the 90 % to 100 % of the CO<sub>2</sub> [100-105] (water is also typically removed through condensation stages). Moreover, recirculating CO and H<sub>2</sub> (reducing agents) diminishes the required amount of coke in the blast furnace, what lowers the CO<sub>2</sub> emissions. Typical capture technologies are vacuum pressure swing adsorption (VPSA) and amine scrubbing. The VPSA presents lower electricity consumption 0.5-0.6 GJ/tCO2 [103,106], but the CO2 streams obtained is not of sufficient purity for permanent storage, thus requiring additional cryogenic distillation to reach 99 % purity (cooling necessities of  $0.1 \text{ GJ/tCO}_2$  [106]. In the case of amine scrubbing, the main disadvantages are the degradation/replacement of the amines, and the requirement of a non-negligible amount of steam to desorb the CO<sub>2</sub> (2.0-4.0 GJ/tCO2 of thermal energy, equivalent to 0.7-1.4 GJ/tCO2 of electricity penalty) [100,107].

In blast furnaces, the top gas can be recirculated not only at the combustion region (i.e., raceways, at the lower tuyeres zone), but also at the beginning of the indirect reduction zone (i.e., shaft, mid zone), at the preparation zone (i.e., preheating, upper zone), or at a combination of them (Fig. 9). Injecting the recirculated gas at the lower tuyeres allow

#### Table 5

Range of values found in the literature for the inlet and outlet streams that can be considered in a typical TGR-OBF process boundary. Not all the inlet streams will necessarily exist in a given process flow diagram.

TGR-OBF process flow diagram	Flow	Temp. (°C)	References
Iron ore (kg/thm)	1450–1730	25	[100,103,106,111,112,127,139]
Coke (kg/thm)	159–468	25	[100,102,103,106,108,112,113,136]
Auxiliary tuyere injections			
PCI (kg/thm)	50-320	25	[100,102,103,106,112,114,136,141]
Natural gas (kg/thm)	42–150	25	[100,109]
COG (Nm <sup>3</sup> /thm)	140	25	[112]
Recycled top gas (Nm <sup>3</sup> /thm)			
Injected in the preparation zone (after combustion)	200–294	1000	[100,109]
Injected in the shaft (after $CO_2$ separation)	82-600	900-1000	
Injected in the tuyeres (after $CO_2$ separation)	60–620	25-1250	[100,103,106,108,111–116]
O (Enriched air		25 1150	[105 108 119]
$O_2$ /Ellicited-all	192 252	23-1130	
$H_{2} O(\alpha/Nm^{3})$	2_60		[100,100,111 140,142]
$N_{2}$ ( $Nm^{3}$ /thm)	2-00		[100,106,111,140,142]
	0-110		[100,100,111-113,117]
Hot metal production (thm/h)	150–570	1350–1500	[21,100,143,102,105,106,108,112,114,116,140]
Slag (kg/thm)	189–364		[100,105,108,111,142]
BFG (before recycling) (Nm <sup>3</sup> /thm)	1030–1447	100-326	[100, 102, 136, 139, 103, 105, 106, 109, 111, 112, 116, 128]
CO (%vol)	23–52		[102, 103, 137, 105, 106, 109, 111, 112, 114, 116, 136]
CO <sub>2</sub> (%vol)	22–48		[102, 103, 137, 105, 106, 109, 111, 112, 114, 116, 136]
H <sub>2</sub> (%vol)	8–26		[102, 103, 137, 105, 106, 109, 111, 112, 114, 116, 136]
H <sub>2</sub> O (%vol)	4–6		[103,111,112,116,136,137]
N <sub>2</sub> (%vol)	1–15		[102,103,105,106,109,111,112,136]
Operating hours (h)	8600		[106]

for a proper interaction between the reducing gas and the solids, but it decreases the flame temperature. Contrarily, injections at mid shaft avoids decreasing the flame temperature, but the peripheral injection leads to a limited penetration and diffusion of the gas to the center of the descending burden (poor solid-gas interaction) [100]. In the case of upper injections, the role of the recirculated gas is only to preheat the descending solids, mitigating the lack of sensible heat that would provide N<sub>2</sub>. As the gas is not aimed to be used as a reducing agent, the diffusion of the gas towards the center is not critical, and the presence of  $CO_2$  is not a problem [100]. Depending on the configuration, the recirculating ratio of the top gas may vary between 30 % and 100 % [100,103,104]. It implies a decrease in the available gases downstream for the I&S plant, and therefore a penalization of 1.5-4.0 GJ/thm in terms of available thermal energy (or 0.5-1.4 GJ/thm in terms of electricity) [100,108]. A potential strategy to palliate this effect is to replace pulverized coal by natural gas, what will increase the H<sub>2</sub> content of the BFG and its calorific value [100]. Typical calorific value of top gas in OBF is 5.7–9.2 MJ/Nm<sup>3</sup>, while in conventional BF is around 3.0 MJ/Nm<sup>3</sup> [102,103,109,110].

To fulfill its role as provider of sensible heat, the recirculated gas is normally injected at 900–1250 °C (in the case of mid and upper injections, at 1000 °C maximum to avoid coke gasification) [100,103,115–117,105,106,108,109,111–114]. To preheat the recirculated gas, pebble-heaters fueled by top gas itself are used (typical heat losses to the ambient are around 5 %) [106]. About 7 % to 12 % of the BFG is used as fuel in the preheating, mixed with other fuels if necessary (e.g., liquefied petroleum gas, natural gas, and/or COG) [103,104,106,110,114]. Hence, this implies an additional decrease on the available thermal energy downstream for the I&S plant of 0.5 GJ/ thm (equivalent to 0.17 GJ/thm of electricity) [106]. Another option could be to heat the  $O_2$ -enriched blast instead of the recirculated top gas, but this solution is not adopted in practice due to technical limitations in the hot stoves (maximum 32 %vol  $O_2$  in the stoves, in order to avoid equipment damage by oxidation), so the  $O_2$  is injected cold at 25 °C [118]. Furthermore, it was shown that at high recycling ratios, is more cost-effective to heat the recycled gas rather than the oxygen blast [118].

In addition to the impact on the available gases (less energy available for self-sufficiency), oxygen blast furnaces also imply greater electricity consumptions in the air separation unit (ASU). The volume fraction of O<sub>2</sub> in the enriched hot blast changes from 0 % to 5 % in conventional BF to 70 % – 100 % in OBF [100,104–106,110–113,117], so the O<sub>2</sub> produced in the ASU increases by 150–280 Nm<sup>3</sup>/thm [106,109,116,119]. Depending on how modern is the technology of the steel plant, the ASU consumption may vary between 260 and 400 kWh/tO<sub>2</sub> [106,109], meaning increments of 0.2 to 0.6 GJ/thm in the electricity consumption.

In total, accounting for all the penalizations ( $CO_2$  separation stage, top gas recycled in the OBF, top gas consumed for heating, and ASU consumption), the thermal energy penalization is 2.0–8.6 GJ/thm, and the electricity penalization is 0.7–1.2 GJ/thm (both combined give an overall equivalent electricity penalization of 1.4–4.2 GJ/thm). Taking into account that integrated steel mills produce only 8.6 to 10.7 GJ/thm of thermal energy in the form of COG and BFG, and that they use between 3.9 and 8.0 GJ/thm of this thermal energy in internal processes (i. e., in coke oven, hot stoves and power plant) [95,109,120–126], the fact of having penalizations associated to OBF of 2.0 to 8.6 GJ/thm may lead to situations of non-self-sufficiency. Therefore, the shortage of available gases is one of the main handicaps of this technology.

#### 5.2. CO<sub>2</sub> emission reduction

Besides providing sensible heat, the recycled top gas acts as reducing agent inside the blast furnace as it is mainly composed by CO and H<sub>2</sub>. This allows to reduce the coke consumption by 14–150 kg/thm, at coke replacement ratios of 0.17-0.25 kg<sub>coke</sub>/Nm<sup>3</sup> (5–34 % decrease with respect to conventional BF) [11,108,110,112,114,127,128]. Although

#### Table 6

Range of values found in literature for different characteristic data of oxygen blast furnaces.

	Value	Reference
Characteristic data of TGR-OBF		
Volume fraction of $O_2$ in enriched air (%)	70–100	[100,104–106,110–113,117]
Percentage of BFG recycled into BF (%)	30-100	[100,103,104]
Percentage of CO <sub>2</sub> captured from the recycled gas (%)	90–100	[100–105]
Percentage of BFG used for heating the recycled gas (%)	7–12	[103,104,106,110,114]
Calorific value of top gas (MJ/Nm <sup>3</sup> )	5.7–9.2	[102,103,109,110]
Thermal reserve zone temperature (°C)	700–950	[100,103,108,127,140]
Chemical efficiency (-)	0.94-0.98	[100,109]
Heat losses (MJ/thm)	230-630	[100,108,110,111,127,137,139]
Percentage of direct reduction (%)	4–19	[103,109,110,129,135,136]
Minimum flame temperature (°C)	1800	[100,108,113,137,138]
Decrease in flame temperature by the recycled gas (°C/Nm <sup>3</sup> )	1.4-5.0	[108,110,114]
Replacement ratio (kg/Nm <sup>3</sup> )	0.17-0.25	[11,108,110,112,114,127,128]
Gas utilization (%)	47.7–54.3	[109,112]
Furnace inner volume (m <sup>3</sup> )	2500-2800	[103,109,140]
Productivity (t/m <sup>3</sup> d)	1.6-8.1	[100,108,112,113,116,135,140,141,144]
Technology Readiness Level (TRL)	2–6	[7,113,131,135,141,144,145]
Cost of retrofitting (M€)	900	[102]
Pay-back (y)	20–30	[146]
Change in performance with respect to air-blown BF		
Increase in $\Omega_2$ production (Nm <sup>3</sup> /thm)	150-280	[106 109 116 119]
Decrease in coke consumption (kg/thm)	14-150	[11 108 110 112 114 127 128]
	11100	[11,100,110,112,11,120]
Decrease in CO <sub>2</sub> emissions (kg/thm)		
Due to recycling	100-500	[100,106,108,112,114,119,129,130]
Due to permanent storage	700–770	[105,106,108,119,131]
Increase in electricity consumption (GJ/thm)		
Due to ASU	0.2–0.6	[106,109,116,119]
Due to carbon capture (VPSA)	0.5–0.6	[103,106]
Decrease in available thermal energy downstream (G1/thm)		
Due to recycling itself	15_40	[100 108]
Due to heating the recycled gas	0.5	[106]
Due to reaching the recycled gas	2 1_4 1	[100 107]
	2.1 1.1	[100,107]
Increase in productivity (%)	25–75	[100,108,112,143,147]
Increase in CAPEX (incl. carbon capture) (M€/(thm/h))	1.25	[146]
Increase in OPEX (t/thm)	76	[146]

some studies report coke consumptions as low as 159 kg/thm, experimentation in prototype-scale oxygen blast furnaces showed 200–230 kg/thm as the minimum feasible coke rate [111].

A direct consequence of this coke saving is the cut in CO<sub>2</sub> emissions. This decrease is inherent to the TGR-OBF technology, and it is in the range 100 to 500 kgCO<sub>2</sub>/thm (typically, 10 % – 40 % reduction with respect to BF) [100,106,108,112,114,119,129,130]. On average, the CO<sub>2</sub> emission reduction found in the literature is around 20 % (Table 8). Additionally, as CO<sub>2</sub> is rejected from the recycled top gas via a capture stage, a non-negligible amount of highly-concentrated CO<sub>2</sub> gas is available for underground storage. Considering that this CO<sub>2</sub> is sent to permanent storage, the total CO<sub>2</sub> emissions reduction can be as high as 800–1270 kg/thm (i.e., up to 86 % reduction) [105,106,108,119,131]. It is worth to mention that all the CO<sub>2</sub> emissions presented in this section are calculated after complete combustion of the gas (i.e., the CO content is accounted as equivalent CO<sub>2</sub>).

An alternative option to take advantage of the captured  $CO_2$  is to combine OBF with Power to Gas (PtG) [121]. PtG technology consumes renewable electricity to produce H<sub>2</sub> via water electrolysis, which is then combined with the  $CO_2$  emissions of the ironmaking process to obtain synthetic methane [132,133]. This synthetic fuel is used in the blast furnace to keep carbon in a closed loop and avoid geological storage [120,134]. The amount of  $CO_2$  that can be avoided through this method

is limited by the mass flow of natural gas that can be injected in the blast furnace, which depends on the flame temperature. About 70–90 kg/thm of CO<sub>2</sub> could be kept in closed loop and prevented from being permanently stored, which represents 5–7 % of the emissions of a conventional BF. However, it implies additional electricity penalizations of 1.3–2.1 GJ/thm, because of the production of renewable H<sub>2</sub> [121].

# 5.3. Operating parameters in OBF

In addition to the process mass flows (Table 5), the operation of a blast furnace is characterized by the percentage of direct reduction, the flame temperature, the heat losses, the temperature of the thermal reserve zone, the chemical efficiency, and the gas utilization (Table 6). All of them present some differences between oxygen blast furnaces and air-blown blast furnaces.

The percentage of direct reduction is between 4 % and 19 % in OBF (in air-blown BF is between 20 % and 40 %) [103,109,110,129,135,136]. The higher the O<sub>2</sub> concentration in the blast, the lower the direct reduction. To a lesser extent, increasing the volume of recycled gas also diminishes the percentage of direct reduction [103]. Moreover, for each Nm<sup>3</sup> of recycled top gas injected at the tuyeres, the flame temperature will be reduced by 1.4–5.0 °C, depending on the temperature of the injected gas [108,110,114]. The amount of gas

Institution	JFE Steel	Minmetals	LKAB	Baowu	Tulachermet
Height (m)	5.1	n/a	6.0	n/a	n/a
Hearth diameter (m)	0.95	1.0	1.4	n/a	n/a
Throat diameter (m)	0.7	n/a	1.0	n/a	n/a
Inner volume (m <sup>3</sup> )	3.9	8.0	8.2	430	1033
Productivity (t/m <sup>3</sup> d)	5.1	5.4-8.1	4.4	n/a	1.6

injected will be limited by the minimum adiabatic flame temperature (AFT) that allows keeping the proper operation of the furnace. The AFT assumed in the OBF studies found in literature is between 1900 and 2800 °C [100,108,137]. This range is actually taken from conventional BF experiences, whose minimum AFT is traditionally assumed at 2000 °C [97]. However, in practice, the lower the percentage of direct reduction, the lower the minimum limit for the flame temperature can be [138]. In fact, some actual blast furnaces have been successfully operated with 1600–1900 °C flame temperatures [113,138]. Since OBFs present remarkably lower percentages of direct reduction than BFs, 1800 °C could be considered as a more realistic technical limit for the flame temperature in OBF [113]. Heat losses for OBF reported in literature are in range 230-630 MJ/thm the [100,108,110,111,127,137,139], which are lower than for BF thanks to the higher productivity and smaller size of the furnace [109]. The temperature of the thermal reserve zone in OBF (700-950 °C) is usually assumed lower than for conventional BF (850-1000 °C), in literature [100,103,108,127,140]. The chemical efficiency used for OBF in the literature is between 0.94 and 0.98 [100], which is higher than that for conventional BF (0.85-0.95) [114] thanks to the downsized hearth diameter, what makes gas channeling effect less relevant [109]. Lastly, the gas utilization for OBF is in the range 47.7 % to 54.3 %, for the studies reviewed [109,112].

# 5.4. Size and productivity

The productivity of a blast furnace is usually restricted by the flooding phenomena, which limits the downward mass flow of a liquid in a bed of solid particles with countercurrent gases. The liquid will stop flowing downwards (or will even rise upwards as reflux), when the gas exerts a limiting force in the opposite direction to the descent of the liquid [148]. Since the OBF presents lower bosh gas flows than conventional BFs, the flooding limitation is less restrictive. In the literature, productivities in the range of 1.6 to 8.1 t/m<sup>3</sup>d are reported (thm per  $m^3$ of inner volume per day) [100,108,112,113,116,135,140,141,144]. In general, the productivity of the OBF is 25 % to 75 % greater than those for conventional BF, what allows to downsize the furnace while keeping the same production rate [100,108,112,143,147]. Conventional BFs have 5000 m<sup>3</sup> inner volume, so OBFs are expected to have around 2500–2800 m<sup>3</sup> inner volume [103,109,140]. Despite of the smaller diameter of the shaft, analysis based on discrete element method showed that the compressive stress on the solids is similar or even lower than in conventional BF [109].

# 5.5. Technology readiness level, and costs

The TGR-OBF technology is not yet commercial. Most of studies found in the literature are TRL 2, and only a few articles mention experimental tests between TRL 3 and TRL 6 (Table 7; note that commercial OBF should have  $2500 \text{ m}^3$  inner volume). Institutions that have performed experimental research on OBF include (in the ascending

order of size) JFE Steel [7,141], the State Key Laboratory of Advanced Steel Processes and Products of China in cooperation with Minmetals Yingkou Medium Plate [135,144], the ULCOS project at LKAB's experimental blast furnace [7], the Baowu Group [135], and Tulachermet [113,135].

The viability of future research and investments in OBF is ruled by the cost of producing 1 ton of steel [146]. The price of steel (without accounting CO<sub>2</sub> taxes) was around 500  $\notin$ /t during the last decade, but it rose to 1400–1800  $\notin$ /t last year due to the global scenario [149]. According to the studies based on pre-pandemic scenarios, the price of steel under OBF technology equals the price of conventional steel when the CO<sub>2</sub> taxes are in the range 40–150  $\notin$ /tCO<sub>2</sub>, depending on the price of electricity and the carbon capture technology (VPSA or amine scrubbing) [102,104,118,146,150]. It should be noted that the electricity price and the CO<sub>2</sub> taxes are correlated, and therefore, it is recommended to consider that electricity price increases by 0.85  $\notin$ /MWh per each 1  $\notin$ /tCO<sub>2</sub> increase in the CO<sub>2</sub> price [146].

Retrofitting BF to OBF is barely considered in literature [102], since the required size of the blast furnace decreases, and O<sub>2</sub>-enrichment above 30 % causes equipment damage in hot air blowing systems (oxidation of metallic pipes, lances, etc.) [100]. Nevertheless, the cost of retrofitting the furnace and piping is estimated at approximately 900 M€ (cost of the carbon capture plant not included) [102]. The investment cost for a new standalone OBF may be smaller than that for a new conventional BF because of its smaller dimensions. However, it implies additional costs related to the larger ASU, compressors, and carbon capture stage. Hence, the overall investment for OBF may be 1.25 M€ greater than that for conventional BF, per thm/h (including carbon capture) [146]. Pay-back on blast furnace investments is assumed to be between 20 and 30 years in the literature [146].

Regarding operating costs, the major differences between the OBF and BF are the amount of coke consumed (up to 150 kg/thm less) and the electricity consumption (up to 4.2 GJ/thm more). Typical costs for coke and electricity are 300  $\notin$ /t and 80  $\notin$ /MWh, respectively [146]. Thus, the OPEX would decrease by up to 45  $\notin$ /thm because of coke savings, but increase by up to 93  $\notin$ /thm due to the electricity consumption (extreme values). Moreover, the transportation and permanent storage of CO<sub>2</sub> can be assumed as an additional cost of 27 %/tCO<sub>2</sub> [146] what translates into 28  $\notin$ /thm. In total, the net increase in OPEX is 76  $\notin$ /thm. At the current price of steel, this represents a 5 % increment in the price of steel (one decade ago, it would correspond to a 15 % increment in the price).

### 6. Pre-combustion CC in BF-BOF

Pre-combustion technologies for carbon capture in the I&S industry can be applied to the CO2 emissions from raw materials preparation, blast furnace, and blast oxygen furnace. The resulting gas stream after CC can be used as fuel in internal combustion processes. The design and integration of chemical absorption, physical adsorption, membrane separation, and sorption enhanced water gas shift (SEWGS) technology



Fig. 10.  $CO_2$  absorption with intercooled absorber (ICA) and rich solvent splitting (RSS), . adapted from [30]

for pre-combustion CC in the BF-BOF route are reviewed in this section.

# 6.1. Pre-combustion with chemical absorption

Certain chemical solvents, such as amine-based (presented in Section 4.1) or aqueous ammonia, can be used for pre-combustion carbon capture. Tobiesen et al. [151] presents one of the early studies based on modelling CO<sub>2</sub> absorption from the off-gases of conventional and oxygen-based blast furnaces using monoethanolamine (MEA), methyl-diethanolamine (MDEA)/piperazine (Pz), and 2-amino-2-methyl-1-propanol (AMP) as primary, tertiary/secondary mixture, and sterically-hindered primary amine solvents, respectively. It is unclear why secondary amines were not tested despite both primary and secondary amines undergo hydrolysis and carbamate mechanisms for  $CO_2$  absorption, as shown in reactions (1) to (7), while tertiary amines only

# undergo slow hydrolysis reaction with CO<sub>2</sub> [152]. *Hydrolysis mechanism:*

$$CO_2 + H_2O \leftrightarrow H_2CO_3(CO_2hydrolysis) \tag{1}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+(Bicarbonate formation)$$
 (2)

$$R_{2} \qquad R_{2}$$

$$| \qquad |$$

$$H^{+} + R_{1} - N \iff R_{1} - N^{+} - H(Acid - basereaction) \qquad (3)$$

$$| \qquad |$$

$$R_{3} \qquad R_{3}$$



Fig. 11. A queous ammonia-based  $\rm CO_2$  capture from the blast furnace of f-gas (BFG) . adapted from [155]

$$R_{2} \qquad R_{2}$$

$$| \qquad |$$

$$CO_{2} + H_{2}O + R_{1} - N \leftrightarrow R_{1} - N^{+} - H + HCO_{3}^{-}(Overall reaction)$$

$$| \qquad |$$

$$R_{3} \qquad R_{3}$$

$$(4)$$

Carbamate mechanism:

(6)

Ultimate Reduction in Steelmaking Process for Cool Earth 50 (COURSE50-2008) in Japan, Pohang Iron and Steel Company (POSCO-2020) program in South Korea, and American Iron and Steel Institute (AISI-2011) program in USA. The ULCOS program focused on the amine scrubbing using MDEA, though it suffers from high energy requirements (about 3.2 GJ/tCO<sub>2</sub>) and further research is needed to reduce the CC energy penalties [11]. The COURSE50 program investigated CO<sub>2</sub> absorption with amines or amines mixed with alcohols/additives. Under this program, Onoda et al. [107] studied 21 solvents such as MEA, MDEA, 2-amino-2-methyl-1-propanol (AMP), 2-Piperidineethanol (2-PPE), diethanolamine (DEA), 2-(ethylamino) ethanol (EAE), N-isopropyldiethanolamine (IPDEA), and 4-piperidineethanol (4PPE). The temperature of adsorbent regeneration was optimised through two pilot plant tests to reduce the CC energy penalty from about 4 to 2 GJ/tCO<sub>2</sub>. However, further studies are needed to understand their degradation and vaporisation losses in the presence of gas contaminants and high temperature over an extended period of time.

The POSCO program recommends aqueous ammonia as solvent for

$$R_{2} \qquad R_{2} \qquad . \qquad R_{2}$$

$$| \qquad | \qquad . \qquad |$$

$$CO_{2} + 2R_{1} - N \leftrightarrow R_{1} - N - C - O^{-} + R_{1} - N^{+} - H(Overall \ reaction)$$

$$| \qquad . \qquad | | \qquad |$$

$$H \qquad . \qquad O \qquad H$$

$$(7)$$

Moreover, AMP also does not favour fast  $CO_2$  absorption, as it hinders carbamate reaction. Since absorption process has high efficiency at low temperature and high pressure,  $CO_2$  capture typically involves four steps: (a) gas pretreatment to reduce temperature and increase pressure through compression, (b) gas absorption with intercooling using alkaline solvent, (c) solvent regeneration by separating  $CO_2$ , and (d)  $CO_2$  compression and drying for transportation. According to the process simulations [151], about 80–90 % of the total energy is needed for steam generation for desorber reboiler, while the remaining 10–20 % drives the gas compressors, blower, and the solvent recirculation pumps. Based on the regeneration energy requirement and the solvent recirculation rate, AMP was the most suitable solvent (reboiler steam consumption: 2.6 MJ/kg<sub>CO2</sub> with MAP, 2.9 MJ/kg<sub>CO2</sub> with MDEA/Pz, and 3.7 MJ/kg<sub>CO2</sub> with MEA), although it would require a large absorber size due to its slow reaction with CO<sub>2</sub>.

To enhance process efficiency and energy savings, heat recovered from BFG or from flue gas of power plant can cover the thermal needs of the amine capture system [30,153]. As it is shown in Fig. 10, an intercooled absorber (ICA) and rich solvent splitting (RSS) was included in the simulation model. The maximum  $CO_2$  capture from BFG was 5 % lower than that from flue gas stream due to the lower  $CO_2$  content in the former. The effect of feed split ratio for minimising solvent regeneration energy and the implications of such designs on the capital cost were not investigated.

Different published works [19,21,154] present overviews of various  $CO_2$  breakthrough programs, including ultra-low carbon dioxide steel making (ULCOS-2004) program in the EU (also discussed in [11]),  $CO_2$ 

absorption process (see Eq. (8)-(12)). A pilot-scale ammonia-based absorption process for  $CO_2$  capture was integrated in an actual I&S plant (Fig. 11) [155].

Aqueous ammonia captures CO<sub>2</sub> through the following reactions:

$$NH_3 + CO_2 + H_2O \leftrightarrow NH_4HCO_3 \tag{8}$$

$$2NH_3 + CO_2 + H_2O \leftrightarrow (NH_4)_2CO_3 \tag{9}$$

$$2NH_3 + CO_2 \leftrightarrow NH_2COOH + NH_3 \leftrightarrow NH_4COONH_2$$
(10)

$$(NH_4)_2 CO_3 + CO_2 + H_2 O \leftrightarrow 2NH_4 HCO_3 \tag{11}$$

 $NH_4HCO_3 + NH_3 \leftrightarrow NH_4COONH_2 + H_2O$  (12)

To avoid ammonia loss with the gas exiting the absorber, the treated gas is water-washed. The CO<sub>2</sub>-loaded solution is regenerated using a reboiler (maintained near 80 °C). The CO2-rich stream from the regenerator is also water-washed to remove ammonia escaping with it. The regenerated ammonia solution is sent to the absorber for its reuse. The regeneration of washing water takes place in the concentrator, where water is separated from ammonia. Through the comparison of CO2 absorption by amines, ammonia, and K<sub>2</sub>CO<sub>3</sub>, it was argued that ammonia would require lowest regeneration energy and absorbent cost with less risk of corrosion and solvent thermal degradation. With a blast furnace off-gas flow rate of 1000 Nm<sup>3</sup>/h, the process was shown to absorb over 95 % CO\_2 (about 10  $t_{\rm CO2}/day)\text{,}$  and produced a gas stream from the regenerator with nearly 99 % CO2. However, an economic analysis and the feasibility of a full-scale plant implementation (with high off-gas flow rate) should be evaluated since the slow rate of CO<sub>2</sub> absorption by ammonia may require a significantly large column size and a high solvent recirculation rate.

Ho et al. [26] studied the retrofitting of existing I&S plants in Australia with  $CO_2$  capture using MEA for  $CO_2$  absorption. Feed pretreatment involved selective catalytic reduction (SCR) to reduce  $NO_x$ concentration below 20 ppm, particulate filter to remove solids, and flue gas desulfurization (FGD) to reduce  $SO_x$  concentration below 20 ppm.



Fig. 12. Process flow diagram of a simple PSA technology, . adapted from [158]

For off-gas with low CO<sub>2</sub> partial pressure, water-gas shift reactor was considered to convert CO to CO2, and thereafter, Selexol (physical solvent) was used for CO<sub>2</sub> absorption [26]. For MEA-based CO<sub>2</sub> capture, the capital and operating cost represented 20-30 % and 70-80 % of the total cost, respectively. Overall, the costs of CO<sub>2</sub> capture were A\$74/tCO<sub>2</sub> for the blast furnace and A\$56/tCO<sub>2</sub> for the Corex process. The CO<sub>2</sub> capture cost for the Corex process could be further reduced to A\$39/tCO<sub>2</sub>, if the inlet gas was compressed to about 20 bar and the water-gas shift reactor was used to enrich the gas with CO<sub>2</sub> so that a physical solvent (Selexol) could be used. Ho et al. [102] extended study [26] by investigating CO<sub>2</sub> capture from Hismelt, Midrex, and mini mill processes. To be costeffective, it was recommended to capture CO2 only from main emission sources (for example, from onsite power plant with cost estimate of A\$76/tCO<sub>2</sub>, coke ovens and stoves with a cost of A\$80/tCO<sub>2</sub>, and sinter plant with a cost of A\$90/tCO<sub>2</sub>) that can achieve CO<sub>2</sub> emission reduction by about 80 % from an I&S industry. Moreover, the use of vacuum pressure swing adsorption (VPSA) with concentrated gas was found to involve lower cost of CO<sub>2</sub> capture than MEA absorption due to lower regeneration energy requirements.

Some studies in the literature provide the comparison of different techniques for  $CO_2$  capture. Quadar et al. [156] compared the efficiency and energy requirements of some  $CO_2$  capture studies from the literature from blast furnace/stove off-gas using aqueous ammonia [155], MEA [26,38], and MDEA/MEA [157], and VPSA [106]. Since the efficiency of

CO<sub>2</sub> capture and energy requirements depend on the gas composition, temperature, pressure, and flow rate, a direct comparison of the results from studies utilizing different feed parameters is difficult. Quadar et al. [156] noted that both absorption and adsorption are suitable for CO<sub>2</sub> capture. Kim et al. [158] simulated PSA and MEA-based absorption processes for CO2 capture from furnace off-gas. The MEA-based absorption process suffered from solvent degradation and loss and equipment corrosion. The absorption process led to a CO<sub>2</sub> stream with higher purity than the PSA process with a difference of 9.95 mol%, but the energy required in the absorption process was 224.78 MW higher than that for PSA. While PSA required lower regeneration energy than the absorption process, its adsorption efficiency was high only when CO<sub>2</sub> was present in high concentrations. Gazzani et al. [29] studied CO<sub>2</sub> capture from an iron & steel plant in the pre-combustion and postcombustion stages using MEA and MDEA solvents, and with sorptionenhanced-water-gas-shift (SEWGS) reactors. The results were presented in terms of specific primary energy consumption for CO<sub>2</sub> avoided (SPECCA, MJ/kg<sub>CO2</sub>) versus % of CO<sub>2</sub> avoided. The pre-combustion CO<sub>2</sub> capture process involved compressing the off-gas, passing it through a water saturator, sending the resultant gas to water-gas shift reactors, and finally, using MDEA-based absorption unit to capture CO<sub>2</sub> and send the H<sub>2</sub>-rich gas to the onsite power plant for combustion. This process, with heat integration, achieved a CO2 avoidance of 89 % with a SPECCA of about 3 MJ/kg<sub>CO2</sub>. In comparison, the processes requiring passing the off-gas from the iron & steel plant to a water saturator and water-gas shift reactors, and thereafter, capturing CO2 using adsorbents and sending the H2-rich gas to the onsite power plant, achieved a CO2 avoidance of 78-89 % with a low SPECCA of about 2.2-2.95 MJ/kg<sub>CO2</sub>.

Onarheim et al. [159] compared the processes involving  $CO_2$  capture using a chemical (MEA) and a physical (Selexol) solvent. A process with a blast furnace using oxygen-enriched air (40 %  $O_2$ ) and a basic oxygen furnace was simulated, where the off-gas was passed through a watergas shift reactor. In comparison to the reference base process (without CCS) with  $CO_2$  emission of 81.6 kg/s, the absorption processes with MEA and Selexol reduced the  $CO_2$  emissions to 34.7 and 24.8 kJ/mol, respectively. The study did not present an economic analysis to understand if the cost associated with physical absorption was lower than that with MEA, as they involved different process equipment.

Chung et al. [160] studied  $CO_2$  capture from the blast furnace off-gas through amine (piperazine) absorption, membrane separation, and hybrids of absorption and membrane separation. A hybrid process required lowest utility and capital costs with operating cost change of \$77 M/ year, capital cost of \$66 M, highest rate of  $CO_2$  avoided (69.4 %), and lowest  $CO_2$  avoidance cost (\$30.4/tCO<sub>2</sub>). Their calculations suggest that the membrane separation unit has a better rate of  $CO_2$  avoided (66.4 %) and a lower  $CO_2$  avoidance cost (\$34.4/tCO<sub>2</sub>) as compared to the amine



Fig. 13. Principle of the PSA CO2-scrubbing techniques (left) and various domains of application and performances of the variant techniques, PSA, VPSA and VSA . adapted from [163]

absorption unit (with their respective values of 61.3 % and 40.6/tCO<sub>2</sub>). However, only one amine (piperazine) was tested to reach this conclusion.

The above studies indicate that  $CO_2$  absorption by amines may be a well-established technique, but VPSA is more suitable for iron & steel plants with less energy demand and lower cost of  $CO_2$  avoidance. This has motivated several adsorption studies, such as by Arasto et al. [106] and Tsupari et al. [146], on  $CO_2$  capture from the oxygen blast furnace, and by Hisashige et al. [161] on  $CO_2$  capture from the smelter off-gas, as discussed in Section 6.2.

The technologies for  $CO_2$  absorption using chemical solvents (e.g., MEA, MDEA) are widely deployed in industries (e.g., for removal of  $H_2S$  and  $CO_2$  from sour gas in natural gas processing facilities), and thus exhibits high TRL (9). However, their application and demonstration to carbon capture from BFG, BOFG, and COG streams at industrial scale has been limited to date. Thus the majority of pre-combustion-based CC technologies reviewed in Section 6.1 are found to be of low TRL (2–4), and to have been investigated solely through simulation rather than experiments, with the exception of a few pilot scale studies conducted as part of either COURSE50, ULCOS, and STEPWISE projects [87,111,144,148,157] for technologies (carbon capture using various amines) or in an independent study [134] for technology (carbon capture using ammonia).

# 6.2. Pre-combustion CC with adsorption processes

In physical adsorption, the main interacting force is the Van der Waals force. In this system, there is no chemical reaction between the gases and the adsorbents, as the gas is physically bonded to the surface of the solid. There are four different ways of regenerating the adsorbent: pressure swing adsorption (PSA), vacuum-pressure swing adsorption (VPSA), temperature swing adsorption (TSA) and electrical swing adsorption (ESA).

A key finding from the ULCOS project indicated that the chemisorption methods such as amine scrubbing, physisorption technologies such as VPSA or PSA, and cryogenics have different domains of optimality, with the concentration of  $CO_2$  in the gas stream to be treated being one of the most critical determining factors [162]. The physisorption schemes are the best in terms of technical performance and cost, both operational and capital, at the concentration levels reported in the BF instance and the TGR-BF scenarios [163]. The technologies for CO<sub>2</sub> capture and separation in the pre-combustion stage with adsorption can be categorized in terms of the adsorbent type (such as alumina, zeolite & MOFs, and activated carbon), regeneration method (such as pressure swing, temperature swing, electric swing, and washing), and type of monolith molecular sieve (e.g., carbon coated substrate and carbon/carbon fiber monolith) [101]. Among these, pressure swing adsorption (PSA)-based techniques have been the most advanced adsorption techniques reported till date. A typical PSA technology involves two stages that could be either operated as a single stage (as shown in Fig. 12) or as dual stage, wherein CO and N<sub>2</sub> are first separated from CO<sub>2</sub> in the first unit packed with a CO<sub>2</sub> adsorbent, such as Zeolite 13X [158] or Zeolum F-9 [164]. Thereafter, the off-gas from the first PSA, consisting mainly of N2 and CO, is introduced to the second unit which accomplishes the separation of CO and N2 using a CO adsorbent [165]. Under plant conditions, the total energy required to recover about 90 % CO2 with a purity of 91 % is ca. 36.9 MW [158]. In addition, a highly-concentrated combustible gas (with 72 mol% of CO and H<sub>2</sub>) is obtained as an exhaust gas byproduct that could be utilized in power generation boilers [158].Fig. 13.

Although high CO<sub>2</sub> recoveries (>90 %) have been reported [158], the purity of CO<sub>2</sub> in the recovered stream is relatively low with PSA technology compared to other CO<sub>2</sub> separation processes. Rao et al. [166] employed a PSA for recovering CO<sub>2</sub> from coke oven gas. The final CO<sub>2</sub> recovered stream contained as much as 24 % moisture, making it unsuitable for compression and storage without further purification. To overcome this demerit, advances in PSA technology have resulted in a combination of other  $CO_2$  mitigation or separation processes with PSA [167]. Another similar technique to PSA is the Vacuum Pressure Swing Adsorption (VPSA) wherein adsorption is carried out at ca. 1.5 bar and desorption is performed under vacuum conditions at 0.05 bar. As the exhaust gas from BF contains moderately high partial pressure of  $CO_2$  (>0.2 bar), VPSA has been shown to be more economical in reducing the  $CO_2$  capture costs [168]. A detailed economic analysis by Ho et al. [102] has shown that VPSA has the potential to reduce  $CO_2$  capture costs by 25–40 % compared to MEA solvent absorption technology.

Two of the key concepts of a top gas recycling blast furnace (TGR-BF) are the removal of  $CO_2$  from the top gas to enhance recycling and injection of oxygen into the furnace in the place of air [169]. In general, the oxygen blast furnace has the benefits of substantially lowering the  $CO_2$  emissions compared to the traditional blast furnace [135]. The net  $CO_2$  emissions from an integrated steel mill combined with a TGR-OBF is about 1.17 t/t crude steel compared to 1.75 t/t crude steel for a process without CCS. Arasto et al. [106] evaluated a VPSA-based  $CO_2$  capture process configuration from the oxygen blast furnace, based on an existing steel facility in Finland.  $CO_2$  emissions are estimated to be reduced between 1.2 and 1.4 Mt/year (from over 4 Mt/year) when CCS is applied to the oxygen blast furnace with and without  $CO_2$  storage, respectively.

TGR-OBF equipped with VPSA for CO<sub>2</sub> capture has also been beneficial for reducing energy consumption of an integrated steel mill (ISM). This technology significantly decreases generation of metallurgy gas in the coking and ironmaking processes (by ca. 53.4 %) which might consequently decrease the electricity output of the power plant. Moreover, the electricity demand of the ISM is ca. 60 % higher than that of the conventional process due to increased consumption by VPSA and oxygen generation plants [103,119]. Thus, additional electricity may have to be generated or purchased for the ISM with TGR-OBF compared with conventional ISM. On the other hand, the energy input to the ISM with TGR-OBF process decreases substantially from 17.89 to 14.67 GJ/t owing to decreased coking coal consumption. It has been demonstrated in the literature that compared to a traditional air blast furnace equipped with TGR, the utilization of a lean grade burden with pulverized coal injection (PCI) and high blast oxygen enrichment (medium, 50 %; enriched 98 %) can curtail carbon consumptions by 14.1 % and 20.2 %, respectively [110,135]. Nevertheless, various strategies for overcoming issues related to low gas volume have been addressed in the literature [130]. Sen [142] proposed a CO<sub>2</sub> accounting procedure based on a carbon balance, which can facilitate evaluation of the recovery of surplus gases to reduce emissions. Carbon capture using VPSA with top exhaust gas recycling was identified as a promising emissions reduction approach. The analysis based on an oxygen blast furnace with top gas recycle configuration developed by ULCOS indicated ca. 90 % reduction in CO<sub>2</sub> content with a CO<sub>2</sub> purity of 87.7 % in the recovered stream. On a commercial scale, VPSA has been successfully implemented in combination with top gas recycling of blast furnace effluent gases [11,111]. While mitigation measures resulted in a 24 % CO<sub>2</sub> emission reduction, nearly 52 % reduction was accomplished with the VPSA technology [11,102]. However, an unsteady state analysis of the TGR-OBF blast furnace have indicated a slightly lower CO<sub>2</sub> emissions reduction (ca. 69 %), and the deviations have been attributed to the differences in CO<sub>2</sub> emission calculation method [128]. Nevertheless, the amount of treated gas recycled into the blast furnace determines the CO<sub>2</sub> reduction levels in the system. For example, at a gas injection rate of 600 Nm<sup>3</sup>/thm, the level of CO<sub>2</sub> emission reduction that could be attained is ca. 1000 kg/ thm. However, when the feed rate is increased to 1100 Nm<sup>3</sup>/thm, the reduction levels increase to about 1200 kg/thm [131].

In addition, the coupling of a cryogenic system with the VPSA results in further purification to attain a higher level of purity (ca. 96.2 % on dry basis) in  $CO_2$  stream, thus making it favourable for transport and storage. In comparison, the level of  $CO_2$  purity attained with PSA and VPSA is about 79.7 % and 87.2 %, respectively. However, the energy



Fig. 14. Separation cost vs  $CO_2$  product purity for the optimal configurations with two, three and four stages (% values in the legend refer to  $CO_2$  recovery). Data from left to right on each series correspond to  $N_2$  residual contents of 1%, 0.5% and 0.1% respectively, . adapted from [162]

consumption for the combined VPSA and cryogenic technique is ca. 2.9 times higher than those for PSA or VPSA systems that could be directly attributed to the energy requirements for  $CO_2$  compression [11]. Another interesting option is the combination of PSA with cryogenic distillation compression that is capable of delivering a 99–100 % pure  $CO_2$  stream [106], with a total energy consumption of 1.12 GJ/tCO<sub>2</sub> compared to 1.05 GJ/tCO<sub>2</sub> for a VPSA + compression and cryogenic system.

An in-situ method for capturing  $CO_2$  by adsorption during the process of COG gasification was proposed by Wang et al. [170]. By integrating the sub-processes of SMR, WGSR, and carbonation in an adsorption enhanced hydrogen amplification reactor (AEHAR),  $CO_2$  was captured using calcium oxide packed in the reactor and later released during the regeneration process. In order to remove other desorbed gases from the recovered  $CO_2$  stream, a hot potassium carbonate process was applied in the downstream section. Since this study focused on maximizing hydrogen recovery, the details on  $CO_2$  recovery and efficiencies were not reported.

Generally, higher adsorption pressure results in a higher recovery ratio, but also in higher blower power consumption. Simultaneously, a lower desorption pressure results in a larger recovery ratio and higher vacuum pump power usage. In an attempt to minimize the recovery cost, Saima et al. [164] experimentally investigated the effects of cycle time and  $CO_2$  concentration in the exhaust blast furnace gas on the efficiency

a) Conventional way



The primary carbon capture technology by adsorption relies on the pressure swing adsorption or vacuum pressure swing adsorption technique. The adsorption process using solid sorbents such as Selexol, alumina, zeolites, and activated carbon, has been demonstrated for several industrial applications (TRL = 9), including hydrogen production in refineries, nitrogen production, and dehydration applications [171]. Most of the studies listed in section 6.2 employ various sorbents in PSA/VPSA with top gas recycling for carbon capture from steel plant off-gases. Nevertheless, since these studies are simulation-based without actual pilot- or plant-scale demonstration, their TRL has been characterized as low (2).

# 6.3. Pre-combustion with membranes

Hasan et al. [172] found that membrane separation is preferable to amine scrubbing when  $CO_2$  concentration in the flue gas is higher than 36 %, which is true for blast furnace off-gas. A wide variety of membrane



Fig. 15. Process flow diagram of a) conventional WGS and b) SEWGS technology, adapted from [179]

b) SEWGS

CO<sub>2</sub>



**Fig. 16.** KPI comparison for different carbon capture technologies: a) termal penalty (MJ/tHM), b) electricity penalty (MJ/tHM) c) cost ( $$/tCO_2$ ), d) CO<sub>2</sub> emission reduction (kg/tHM), e) CO<sub>2</sub> purity (%) and f) TRL (-). Nomenclature: Post-Chem is postcombustion carbon capture (CC) by chemical absorption; Post-Memb is postcombustion CC by membranes; CaL is calcium looping; ChL is chemical looping; OthL is other looping processes; Oxy-TGR is oxy-blast furnace with top gas recycling (TGR); Pre-Chem is precombustion CC by chemical absorption; Pre-Adsor is precombustion CC by adsorption; Pre-Memb is is precombustion CC by membranes and SEWGS is sorption enhanced water gas shift.

materials including polymers [160,162,173–175] and zeolites [176] have been employed for CO2 recovery from various industrial waste gases, among which polymeric membranes are largely preferred for coke oven gas and blast furnace gas. Lie et al. [174] compared the performance of a fixed site carrier membrane (FSCM), comprised of amine groups in the polymeric backbone, with carbon based membranes. The results showed that aminated polymeric membranes exhibited enhanced permeability and selectivity in favour of CO<sub>2</sub>. Moreover, while the presence of moisture in the blast furnace top gas stream is detrimental for carbon-based membranes, it is beneficial for FSCM as the active amine groups act as carriers for CO2-water complex. Membrane Technology Research (MTR)'s Polaris<sup>®</sup> membrane has been the most widely employed one in lab and pilot-scale CO2 capture studies as it possesses the highest CO2 Gas permeance unit (GPU) of 1000, CO2-N2 selectivity of 50, and CO<sub>2</sub>-CO selectivity of more than 67 measured at 10 °C [177] in addition to higher stability. Such improvements in membrane selectivity have enabled development of novel CO2 capture concepts in subambient conditions using membrane-hybrid cryogenic processes. However, simulation studies have demonstrated that such hybrid techniques are economically suitable only for high-CO<sub>2</sub> content flue gas, and not significant for lean CO<sub>2</sub> streams like BF and COG [178].

CCU from BF or BOF process off-gas by polymeric membranes typically requires multi-staged operation to meet the desired  $CO_2$  recovery and purity levels, owing to the inherent limitations of the solutiondiffusion separation mechanism [162]. An advanced superstructure design with unrestricted stream connections and interlooping proposed by Santos et al (2018) [162] demonstrates the feasibility to minimise overall  $CO_2$  recovery cost by optimising numerous membrane architectures parameters, including number of stages, downstream pressure, membrane surface area, and stream connections.

The effect of CO<sub>2</sub> recovery and residual N<sub>2</sub> constraints on separation cost has been reported in a few studies [160,162,173–175]. The desired CO<sub>2</sub> product purity is significantly higher for MTR's Polaris membrane due to its high CO<sub>2</sub>-N<sub>2</sub> selectivity. CO<sub>2</sub> concentration and recovery are also influenced sharply by the number of membrane stages considered in the study. In fact, even with a high CO2/CO selectivity, a high level of CO<sub>2</sub> purity (>95 %) cannot be achieved by a single membrane unit. A three-staged membrane reactor setup connected in series could reduce CO concentration in the exit gas below 0.2 % [160]. Further, it is possible to achieve product streams with very low  $N_2$  content (0.1–1 %) using a superstructure design as demonstrated by Santos et al 2018 [162]. Nevertheless, it has been shown that at fixed recoveries, decreasing N<sub>2</sub> residual content, say from 1 % to 0.1 % in the CO<sub>2</sub>-rich product stream would increase separation cost, although the reverse (increasing recovery at constant purity) has a less pronounced effect [162].

It could be expected that increasing the number of membrane stages may increase the overall CO<sub>2</sub> separation cost. Based on a global optimisation procedure employing a non-linear programming formulation of the multistage superstructure design, the influence of CO<sub>2</sub> purity and number of membrane stages on separation costs was investigated and has been illustrated in Fig. 14 [162]. It can be noted that when high recovery and/or purity are required, three-stage setups were optimum in reducing separation costs and projected to be in the range of 32–50  $/tCO_2$ . The third stage is utilised to collect CO<sub>2</sub> from the retentate of the first stage for CO<sub>2</sub> recoveries of 95–99 % and 0.5 % N<sub>2</sub> concentration. In the 90–99 % recovery range, a three-stage cascade was the optimum arrangement for a 0.1 % N<sub>2</sub> content. Separation costs were not significantly reduced in process designs with four membrane stages.Fig. 15.

The effect of effluent gas composition on  $CO_2$  recovery and associated costs could be analyzed from the works of Lie et al. [174] and Chung et al. [160]. The variations in the furnace off-gas composition could result from the type of reducing gas (air or oxygen) used for combustion reactions. Generally, a decreased nitrogen content in the feed stream (oxygen as RG) improves the  $CO_2$  flux through the membrane that results in increased recovery percentages. However, the resulting increased CO<sub>2</sub> handling volume increases the membrane section duty by about 66 % relative to the conventional air-driven blast furnace [174]. On the other hand, considering the expander energy and other associated costs involved in the two processes, the difference in overall CO<sub>2</sub> recovery costs remains quite similar. The relatively higher recovery cost (ca. 34.4 \$/tCO<sub>2</sub>) reported by Chung et al. in comparison to Lie et al. is due to the higher CO<sub>2</sub> purity levels considered in the product stream. In addition, the presence of impurities (NO<sub>x</sub>, SO<sub>x</sub> and H<sub>2</sub>S) in the effluent stream tends to deteriorate the membrane performance with time. Sensitivity studies on the membrane permeability values and CO<sub>2</sub> selectivity ratio indicated that a 50 % reduction in overall membrane permeability resulted in a 10 % increase in separation cost, whereas a 50 % reduction in CO<sub>2</sub> selectivity resulted in a 34 % increase [160].

Among all membranes including polymers and zeolites, Membrane Technology Research (MTR)'s Polaris© membrane has been widely tested for carbon capture in lab and pilot-scale studies. Technology development for pre-combustion CC with membranes has mainly focused on the optimization of the number of stages and process configuration in a superstructure-staged membrane process. While the single-staged process has been validated at lab-scale (TRL = 4) [175], most of the multistage processes have been investigated using modelling and simulation (TRL = 2) [160,162,173,174]. The technology for other concepts including membrane process coupled with cryogenics [178] has also been demonstrated only in simulations.

# 6.4. Pre-combustion with SEWGS

Sorption enhanced water gas shift (SEWGS) technology combines pre-combustion carbon capture via adsorption and hydrogen production from syngas via WGS reaction in a single process capsule [179]. The catalyst used for the WGS reaction also serves to adsorb the CO2 generated by the WGS reaction. Among various catalytic materials, potassium carbonate hydrotalcite-based materials are the most common [29,45,179] and technically advanced in terms of dual efficiency. While other commercial iron-based high-temperature catalysts have been tested for WGS reaction, CO2 adsorptive performance has not been assessed [180]. However, regeneration of the sorbents is highly energyintensive and thus necessitates efficient thermal integration techniques, like Ca-Cu chemical looping [93] and pressure release followed by steam purging using a PSA approach [29,32]. The demand for steam by the WGS reaction and SEWGS rinse/purge is responsible for the CO<sub>2</sub> capture energy penalty. Hence different configurations, such as expander layout, and saturator layout, focusing on heat integration between steam cycle and SEWGS have been investigated in the literature [32,45].

A common method to provide the SEWGS reactor with the precise wet gas composition and reduce steam purge during regeneration is incorporating a pre-shift WGS reactor prior to the SEWGS unit [45,179]. For the pre-shift reactor, a Johnson Matthey catalyst has been proven to reduce CO concentration in the BFG effluent stream from 20 % to 5 % [179]. It has been demonstrated that integrating SEWGS for both exhaust gas recycling and power generation section reduces overall CO2 plant emissions by nearly 85 % compared to only 50 % for power generation section of steel industry [32]. In particular, the treatment of effluent gases (BFG, BOFG, and COG) using SEWGS could curtail CO2 emissions by 80-90 % [29,32,93]. Furthermore, sorbent reusability studies estimated a 12 % decrease in CO2 avoidance efficiency between fresh and thousands of cycles-old material [29], which is negligible considering the lifetime and cost of the material. In comparison to other amine-based technologies, SEWGS exhibits the highest energy efficiency (ca. 37.7 %) and lowest specific primary energy consumption ca. 2.2 MJ/kg<sub>CO2</sub>) [29].

The technology for pre-combustion CC with SEWGS has been demonstrated in a pilot-scale facility (14 t/d  $CO_2$  removal rate) using BFG as part of the STEPWISE project (TRL = 6) [157, [181]. However, investigations focused on either process modification to SEWGS or their



Fig. 17. Cost of CC as a function of CO<sub>2</sub> emission reduction, by carbon capture technology. Nomenclature identical to Fig. 16.

applications to other steel plant off-gases (i.e., other than BFG) [30,43,27,74] is currently at low TRL (2).

#### 7. Carbon capture technologies comparison

A comparison of all carbon capture technologies is presented here with respect to 6 different KPIs: thermal penalty ( $MJ/kgCO_2$ ), electrical penalty ( $MJ/kgCO_2$ ), economic cost ( $$/tCO_2$ ), CO<sub>2</sub> emission reduction ( $kgCO_2/tHM$ ), CO<sub>2</sub> purity (%) and TRL (-). The results of this comparison are compiled in Fig. 16. In order to provide a holistic insight, the

minimum and maximum values, as well as the average and all the sampling found from all the reviewed scientific works, are included in Fig. 16. Such a representation highlights differences in the presence of each technology in the bibliography.

For oxy blast furnaces with top gas recycling (oxy-TGR) technology, only the decrease of  $CO_2$  because of injecting TGR is accounted for, and not the decrease that would be achieved by storing underground the pure  $CO_2$  from the CC stage. However, pre-combustion with adsorption (pre-adsor) technology is usually coupled with oxy-BF and TGR, and the combined benefit is taken into account for this technology.



Fig. 18. Electricity penalty as a function of CO<sub>2</sub> emission reduction, by carbon capture technology. Nomenclature identical to Fig. 16.



Fig. 19. Number of scientific papers published, organised by year and technology. Nomenclature identical to Fig. 16.

The thermal penalty ranges between 1.3 and  $6.2 \text{ MJ/kgCO}_2$  for postcombustion chemical absorption (post-chem), calcium looping (CaL), other looping processes (OtherL) and pre-combustion chemical absorption (pre-chem); in contrast oxy-TGR stands out with 0.3–0.8 MJ/kgCO<sub>2</sub> of thermal energy consumption. Even more, Jin et. Al. [119] calculates a negative penalty (i.e. there is an excess of available energy) of -13.4MJ/kgCO<sub>2</sub>. Other technologies such as post- and pre-combustion with membranes (post-memb and pre-memb), chemical looping (ChL), preadsor and sorption enhanced water gas shift (SEWGS) do not have thermal consumption or the data was not available (n/a).

Regarding the electricity penalty, the ranges are wider. Post-chem, CaL and pre-chem are the technologies with the lower electricity consumption, with less than 1 MJ/kgCO<sub>2</sub> on an average. This is due to the process energy consumption being mainly thermal, with a marginal electricity consumption related to the CO<sub>2</sub> compression (up to 100–150 bar). Post-memb, pre-memb, SEWGS and pre-adsor are technologies that compress the gases to capture CO<sub>2</sub>, and therefore have a higher electricity penalty between 1 and 3 MJ/kgCO<sub>2</sub> on an average. Post-memb has an outliner data much higher than the rest (4.4 MJ/kgCO<sub>2</sub>, when the average is 1.8 MJ/kgCO<sub>2</sub>). This study corresponds to sinter flue gas capture, which has a very low CO<sub>2</sub> content that provokes higher compression consumptions. Oxy-TGR has the wider range of electricity penalty of all technologies due to the great variety of configurations available to implement this technology, from less than 1 MJ/kgCO<sub>2</sub> to more than 8 MJ/kgCO<sub>2</sub>.

The bulk of published economic analyses have focused on post-chem technology, with more than 19 samplings compared to other technologies that combine less than 7 samplings. This technology as well as oxy-TGR and pre-chem have the higher average economic cost, with approximately 70 \$/tCO<sub>2</sub>, while other technologies range between 30 and 60 \$/tCO<sub>2</sub>. It is important to notice that only three studies have performed economic analyses for CaL technology, only one study for SEWGS technology, and none for ChL and OtherL. This highlights a lack of economic analyses in this area. The potential CO<sub>2</sub> mitigation is very high, especially if it is considered that typical emissions from the BF-BOF route range between 2000 and 2200 kgCO<sub>2</sub>/tHM. Nevertheless, most of the published works are simulations with a low TRL, and therefore they do not take into account the physical or economical constraints of actual

facilities. So far, the maximum  $CO_2$  amount captured has been 1270 kg $CO_2$ /tHM, reached under TRL 6 in a pilot plant in Lulea (Sweeden), within ULCOS project [131]. They focused on an experimental oxy-blast furnace with top gas recycling and VPSA to capture the  $CO_2$ .

Only one technology achieves a  $CO_2$  purity lower than 90 %, which is the pre-adsor, with an average of 88 % and a minimum of 80 %. From the remaining technologies, only membranes have an average value lower than 95 % for economic reasons. Many of the technologies analysed have a TRL 6, such as post-memb, oxy-TGR, pre-chem, pre-adsor and SEWGS; nevertheless, most studies are simulations with TRL 2. Thus, only 11 published works belong to TRL 6, 5 belong to TRL 5, and 101 belong to TRL 2–4.

In order to clarify the interrelations between specific economic costs and CO<sub>2</sub> mitigation potential, both KPIs are represented in Fig. 17. Additionally, the space defining the range for each KPI in the reviewed works is highlighted. Firstly, the shape of the coloured regions allows distinguishing the most investigated technologies from those with scarce data. Specifically, the natural trend should be the lower CO<sub>2</sub> reduction, the lower specific cost. Such behaviour is only exhibited by the pre- and post-chem technologies. This is an expected result as it is the only commercial technology of carbon capture, at least in the power sector. Secondly, the two works related to CaL present very different specific costs. This difference is due to the consideration or not of different issues, i.e. Tian et. al. [66] considers retrofitting of an existing lime kiln, cutting costs and directly capturing calcination CO<sub>2</sub>, while Cormos et. al. [39] considers natural gas as a fuel in the calciner instead of coal. Therefore, it can be concluded that it could be a very promising and competitive technology, but further research is needed to corroborate the results. According to the available data, oxy-TGR is expensive and the CO<sub>2</sub> mitigation potential is limited, which is because the CO<sub>2</sub> decrease accounted only takes into account oxy and TGR, and not the CO<sub>2</sub> from the carbon capture stage. Finally, further research is required for pre-adsor, pre-memb and SEWGS to generate sufficient and reliable data, as only one published data is available for each one. Also, postmemb, ChL and OtherL need further research, because no study was found that carried out a technical and economic analysis in the same paper.

The interrelation between electricity penalty and CO<sub>2</sub> mitigation

# Table 8

Main KPIs for reviewed CC technologies.

Method/ Technology	Source	Thermal Penalty	Electrical Penalty	Cost	CO <sub>2</sub> emission reduction	Total CO <sub>2</sub> produced <sup>c)</sup>	CO <sub>2</sub> purity	TRL	Year	Country	Ref.
-	-	MJt∕ kgCO₂	MJe∕ kgCO₂	\$/tCO <sub>2</sub>	kgCO <sub>2</sub> /tHM	kgCO <sub>2</sub> /tHM	%	-	-	-	-
3.1. Post combu	stion CC with chen	nical absorptio	on								
MEA	BF flue gas	n/a	n/a	78.5 <sup>a)</sup>	n/a	n/a	n/a	2	2011	Australia	[24]
MEA	Coke oven	n/a	n/a	85.6 <sup>a)</sup>	n/a	n/a	n/a	2	2011	Australia	[24]
MEA	Hot Stoves,	3.0 - 6.2	n/a	n/a	n/a	n/a	greater	2	2019	Romania	[34]
	Power plant,						than95				
	Coke oven,										
	Lime kiln	0.7	-	- /0	<b>n</b> /a	- /2	<b>=</b> /a	4	2010	Toimon	1051
and P7	HOL SLOVES	3.7	II/ d	II/ d	11/ a	11/ d	11/ d	4	2010	Talwall	[23]
MEA	Power plant	38-41	n/a	n/a	n/a	n/a	n/a	2	2015	Switzerland	[29]
MEA	BF flue gas	n/a	1.5 <sup>a)</sup>	68 <sup>a)</sup>	2.7 Mt/vear	n/a	n/a	2	2010	Australia	[26]
MEA	BF flue gas	4.5-6.5	n/a	n/a	n/a	n/a	n/a	2	2017	Taiwan	[27]
MEA	BF flue gas	4.2	n/a	n/a	1 t/day	n/a	n/a	5	2011	Japan	[28]
RITE-A	BF flue gas	3.3	n/a	n/a	1 t/day	n/a	n/a	5	2011	Japan	[28]
RITE-B	BF flue gas	3.1	n/a	n/a	1 t/day	n/a	n/a	5	2011	Japan	[28]
MEA	Power plant	3.1	0.4 <sup>a)</sup>	n/a	n/a	n/a	n/a	2	2018	Sweden	[30]
MDEA	Hot Stoves,	2.9	n/a	76–80 <sup>a)</sup>	1259	2093	greater	2	2016	Romania	[35]
	Power plant,						than95				
	Coke oven,										
	Lime kiln										
MEA	Power plant,	3.2	n/a	48.8 <sup>a)</sup>	n/a	1700	n/a	2	2019	Sweden	[36]
	Hot stoves,										
	BFG										
MEA	Power plant	3.0	n/a	n/a	688	1625	n/a	2	2018	Spain	[31]
MEA	<b>II</b> + 0:		n/a	n/a	230	2093	n/a	2	2019	Romania	[45]
MEA	Hot Stoves,	3.4	0.4 4	92–204 <sup>a</sup>	n/a	n/a	n/a	2	2013	Finland	[37 38]
MEA	Power plant	4.1	- 1-				- 1-	0	0010	111/	5001
MDEA	Coke Oven	4.1	n/a		n/a 1050	n/a	n/a	2	2018	UK Domonio	[33]
MDEA	Hot Stoves,	3.1	n/a	80.9	1259	2093	n/a	2	2020	Romania	[39]
	Coke oven										
	Lime kiln										
MFA	Power plant	48	n/a	38 2 <sup>a)</sup>	369	2016	100	2	2020	Italy	[32]
MEA	Hot Stoves	n/a	n/a	46–90 <sup>a)</sup>	n/a	n/a	n/a	2	2013	Finland	[40]
	Power plant	11/ 4	ii, u	10 50	, u	11/ u	11/ U	-	2010	1	[ 10]
MDEA	Coke oven.	n/a	n/a	n/a	n/a	n/a	98.8	2	2021	Romania	[41]
	Lime kiln, BOF										
MEA	Sintering	3.5	0.28 <sup>a)</sup>	84.9 <sup>a)</sup>	n/a	n/a	n/a	2	2021	S. Korea	[42]
MEA	Coke oven	3.3	0.28 <sup>a)</sup>	69.9 <sup>a)</sup>	n/a	n/a	n/a	2	2021	S. Korea	[42]
MEA	Lime kiln	3.3	0.28 <sup>a)</sup>	72.2 <sup>a)</sup>	n/a	n/a	n/a	2	2021	S. Korea	[42]
MEA	Power plant	2.9	0.28 <sup>a)</sup>	63 <sup>a)</sup>	n/a	n/a	n/a	2	2021	S. Korea	[42]
MEA	Hot stoves	2.9	0.28 <sup>a)</sup>	65.6 <sup>a)</sup>	n/a	n/a	n/a	2	2021	S. Korea	[42]
MEA	-	4.4	0.78 <sup>a)</sup>	53.8 <sup>a)</sup>	800	1800	n/a	2	2021	The Nether.	[43]
MDEA/PZ	Hot Stoves,	2.3	0.6 <sup>a)</sup>	97 <sup>a)</sup>	1700	2200	n/a	2	2021	The Nether.	[44]
	Power plant,										
	Coke oven,										
	Lime kiln										
3.2. Post combu	stion CC with mem	branes									
Polaris	Power plant,	n/a	0.9–1.0 <sup>a)</sup>	36–47 <sup>a)</sup>	n/a	n/a	99	6	2018	USA	[59]
	Hot stoves										
PVAm	Power plant,	n/a	1.2 <sup>a)</sup>		n/a	n/a	95.5	3	2021	Romania	[41]
	Hot stoves										
Polyimide	Sintering	n/a	4.4 <sup>a)</sup>	252.7 <sup>a)</sup>	n/a	n/a	90	3	2021	S. Korea	[42]
Polyimide	Coke oven	n/a	1.7 <sup>a)</sup>	91.2 <sup>a)</sup>	n/a	n/a	90	3	2021	S. Korea	[42]
Polyimide	Lime kiln	n/a	1.4 <sup>a)</sup>	83.3 <sup>a)</sup>	n/a	n/a	90	3	2021	S. Korea	[42]
Polyimide	Power plant	n/a	1.2 <sup>a)</sup>	54 <sup>a)</sup>	n/a	n/a	90	3	2021	S. Korea	[42]
Polyimide	Hot stoves	n/a	1.2 <sup>a)</sup>	52.5 <sup>a)</sup>	n/a	n/a	90	3	2021	S. Korea	[42]
4.1. Looping CO	C with calcium loop	ing									
CaO-CaCO3	BFG, BOFG,	2.9	0.5	60.2	1023-1709	2090	95	2	2016	Romania	[35]
	hot stoves, lime			€/tHRC							
	kilns, COG										
CaO-CaCO3	Hot stoves,	2.7	0.1 <sup>a)</sup>	N.A.	1337–1567	2090	95	2	2019	Romania	[34]
	BFG, BOFG,										-
	COG, lime kiln										
CaO-CaCO3	Hot stoves,	n.a.	0.6	73.8 <sup>a)</sup>	1450	2090	95	2	2020	Romania	[39]
	BFG, BOFG,										
	COG, lime kiln										

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# Table 8 (continued)

Method/ Technology	Source	Thermal Penalty	Electrical Penalty	Cost	CO <sub>2</sub> emission reduction	Total CO <sub>2</sub> produced <sup>c)</sup>	CO <sub>2</sub> purity	TRL	Year	Country	Ref.
	_	MJt∕ kgCO₂	MJe∕ kgCO₂	\$/tCO <sub>2</sub>	kgCO <sub>2</sub> /tHM	kgCO <sub>2</sub> /tHM	%	-	-	-	-
3.1. Post combu	stion CC with che	emical absorptio	n								
CaO-CaCO3	COG	4.2–5.6	n.a.	n.a.	68071 t/year	68400 t/ vear	high- purity	3	2017	China	[62]
CaO-CaCO3	BFG	n.a.	n.a.	n.a.	n.a.	n.a.	high- purity	3	2014	Israel	[63]
CaO-CaCO3	BFG, COG	2.7	2.5 <sup>a)</sup>	13–17 <sup>a)</sup>	1422	1800	high- purity	3	2018	China – UK	[66]
4.2. Looping CC	with chemical lo	oping									
e2O3-FeO	COG	n/a	n/a	n/a	n/a	n/a	n/a	2	2018	China	[81]
e2O3-FeO	Sinter plant	n/a	n/a	n/a	n/a	n/a	n/a	3	2020	UK	[80]
e2O3-FeO	COG	n/a	n/a	n/a	1771–2280 kmol/h	n/a	90	4	2018	China	[79]
JiO-Ni	COG	n/a	n/a	n/a	n/a	n/a	n/a	4	2018	China	[76]
.3. Looping CC	with other looping	ng processes									
a-Cu	BFG	1.4–1.7	n/a	n/a	n/a	n/a	57–99.9	4	2020	Spain	[91]
Ca-Cu		n/a	n/a	n/a	n/a	n/a	n/a		2019	Spain	[90]
a-Cu. (COG)	BFG, COG	2.6	n/a	n/a	502	1619	97.4	4	2018	Spain	[31]
Ca-Cu. (COG + NG)	BFG, COG	4.3	n/a	n/a	1618	1619	97.4	4	2018	Spain	[31]
CaCO3/FeO- CaO/Fe2O3	BFG	n/a	n/a	n/a	n/a	n/a	n/a	4	2016	China	[92]
AgO/MoO3- MgCO3/ Mac2	BFG	n/a	n/a	n/a	n/a	n/a	n/a	3	2020	China	[94]
a-Cu + SEWGS	BFG, BOFG, COG	n/a	n/a	n/a	617	1922	96.8	5	2017	Spain	[93]
Dxy-BF + TGR Dxy-BF +	BFG BFG	0.3 n/a	5.6 n/a	50–90 n/a	462 <sup>b)</sup> 550 <sup>b)</sup>	1244 1320	n/a n/a	2 2	2014 2004	Finland Japan	[106 14 [108]
TGR Dxy-BF +	BFG	0.8	1.7	n/a	273 <sup>b)</sup>	1367	n/a	4	2015-2016	Japan	[100109
TGR Dxy-BF +	BFG	n/a	n/a	n/a	176 <sup>b)</sup>	1330	n/a	2	2021	Spain	111] [121]
TGR + PtG Dxy-BF +	BFG	n/a	0.6	n/a	374 <sup>b)</sup>	1338	n/a	2	2004	Korea	[182]
TGR Dxy-BF +	BFG	n/a	1.4	90	420 <sup>b)</sup>	2420	n/a	2	2013	Australia	[102]
Dxy-BF +	BFG	n/a	0.98	n/a	218 <sup>b)</sup>	1377	n/a	2	2016	China	[112]
Dxy-BF +	BFG	n/a	n/a	n/a	489 <sup>b)</sup>	1429	n/a	2	2016	China	[103]
)xy-BF + TGB	BFG	-13.4	8.1	n/a	240 <sup>b)</sup>	2066	n/a	2	2015	China	[119]
)xy-BF + TGB	BFG	n/a	n/a	n/a	n/a	n/a	n/a	2	2019	Japan	[161]
Dxy-BF + TGR	BFG	n/a	n/a	n/a	181 <sup>b)</sup>	1267	n/a	2	2010	China	[127]
Dxy-BF + TGB	BFG	n/a	n/a	n/a	n/a	n/a	n/a	4	2018	China	[139]
oven	COG	n/a	n/a	n/a	n/a	n/a	n/a	3	2020	China	[183]
xy-BF + TGR	BFG	n/a	n/a	n/a	184	1397	n/a	2	2020	China	[184]
xy-BF + TGR	BFG	n/a	n/a	n/a	167 <sup>b)</sup>	1450	n/a	2	2010	Finland	[104]
xy-BF + TGR	BFG	n/a	n/a	58.5	390	1600	n/a	2	2010	Finland	[105]
xy-BF + TGR	BFG	n/a	n/a	n/a	100	n/a	n/a	2	2015	Finland	[114]
xy-BF + TGR	BFG	n/a	n/a	n/a	367 <sup>b)</sup>	1547	n/a	2	2015	India	[110]
xy-BF + TGR	BFG	n/a	n/a	n/a	401 <sup>b)</sup>	1670	n/a	6	2009	Sweden	[16913] 115]
)xy-BF + TGB	BFG	n/a	n/a	n/a	506 <sup>b)</sup>	1701	n/a	2	2017	China	[129]

(continued on next page)

# Table 8 (continued)

Method/ Technology	Source	Thermal Penalty	Electrical Penalty	Cost	CO <sub>2</sub> emission reduction	Total CO <sub>2</sub> produced <sup>c)</sup>	CO <sub>2</sub> purity	TRL	Year	Country	Ref.
	_	MJt∕ kgCO₂	MJe∕ kgCO₂	\$/tCO <sub>2</sub>	kgCO <sub>2</sub> /tHM	kgCO <sub>2</sub> /tHM	%	-	_	_	-
.1. Post combu	stion CC with chem	nical absorptio	n								
xy-BF + TGB	BFG	n/a	n/a	n/a	166 <sup>b)</sup>	1305	n/a	2	2016	China	[128]
Dxy-BF + TGR	BFG	n/a	n/a	n/a	159 <sup>b)</sup>	1330	n/a	2	2017	China	[130]
Dxy-BF + TGR	BFG	n/a	n/a	n/a	279 <sup>b)</sup>	1305	n/a	2	2017	China	[185]
Dxy-BF + TGB	BFG	n/a	n/a	n/a	-7.5 <sup>b)</sup>	1436	n/a	2	2004	Japan	[137]
Dxy-BF +	BFG	n/a	n/a	n/a	-27 <sup>b)</sup>	1408	n/a	2	2005	Japan	[116]
Dxy-BF + TGR	BFG	n/a	n/a	n/a	247 <sup>b)</sup>	1379	n/a	2	2010	Japan	[186]
.1. Pre combus	stion CC with chem	ical absorption	n								
GR-BF + PZ	BFG	2.4	0.2 <sup>a)</sup>	40.6 <sup>a)</sup>	777	1268	95	2	2018	Korea	[160]
inspecified	BFG	2	n/a	n/a	n/a	n/a	90	6	2016	Japan	[165]
ΛĒĀ	BFG, BOFG, COG	3.1	0.4 <sup>a)</sup>	62 <sup>a)</sup>	130 t/h	141 t/h	99	2	2015	Korea	[158]
NH3	BFG	2.5	n/a	n/a	9.3 t/day	10.3 t/dav	99	6	2014	Korea	[155]
GR-BF + MEA	BFG	n/a	1.4–1.5 <sup>a)</sup>	86–97 <sup>a)</sup>	520-640	n/a	n/a	2	2013	Australia	[102]
JLCOS-MDF.A	BFG	3.2	0.61 <sup>a)</sup>	n/a	n/a	n/a	n/a	_	2010	France	[163]
IEA	BFG	n/a	n/a	n/a	564	n/a	n/a	2	2019	Sweden	[153]
IEA	BFG	3	0.4 <sup>a)</sup>	n/a	n/a	n/a	n/a	2	2018	Sweden	[30]
nspecified	BFG	2	n/a	n/a	n/a	n/a	n/a	6	2016	Janan	[107]
IISPECIALE IFA	BEG BOEG	13	$12^{a}$	n/a	673	961	n/a	2	2016	Finland	[159]
IDEA	BFG, BOFG,	2.9	n/a	n/a	1192 g/kWel	1339 g/	98.6	2	2015	Italy	[29]
AE A	BEC	4.4	n/2	69 a)	1048	1199	n/2	2	2011	Australia	[26]
	DFG	4.4	II/a	08	1040	1100	11/a	2	2011	Norman	[20]
PZ and AMP	brg	2.2-2.4	11/ a	11/ a	11/ a	11/ a	90-97	2	2007	Norway	[131]
5.2. Pre combus	stion CC with adsor	ption	a ( a)								
GR + VPSA	OBFG	n/a	0.4	n/a	860	1650	n/a	2	2016	Malaysia	[101]
PSA	BFG	n/a	n/a	n/a	3 t/day	3.8 t/day	99.5	6	2016	Japan	[165]
SA	BFG, BOFG, COG	n/a	1.0 *	38 "	130 t/h	141 t/h	91.2	2	2015	S. Korea	[158]
GR-VPSA	BFG	n/a	0.9–1.0 <sup>a)</sup>	59–60 <sup>a)</sup>	520-580	n/a	n/a	2	2013	Australia	[102]
/PSA	BFG	n/a	1.1 <sup>a)</sup>	n/a	n/a	n/a	n/a	2	2010	France	[163]
GR + VPSA	OBFG	n/a	0.9	n/a	2.7 Mt/a	3.2 Mt/a	92	2	2014	Finland	[106]
GR + VPSA	BFG	n/a	n/a	n/a	1794	1900	87.7	2	2013	India	[142]
PSA	BFG	n/a	0.4 <sup>a)</sup>	n/a	6.3 t/day	7.8 t/day	n/a	5	2013	Japan	[187]
GR + VPSA	BFG	n/a	n/a	n/a	1270	1671	n/a	6	2009	Sweden	[131]
GR + VPSA	OBFG	n/a	n/a	n/a	n/a	n/a	n/a	2	2017	China	[130]
GR + VPSA	OBFG	n/a	2.7 <sup>a)</sup>	n/a	1540	2080	n/a	2	2017	China	[119]
GR + VPSA	OBFG	n/a	10.4 kJ∕ thm	n/a	701	1485	n/a	2	2016	China	[103]
GR + VPSA	OBFG	n/a	0.4 <sup>a)</sup>	n/a	860	1650		6	2016	Malaysia	[11]
GR + VPSA	BFG	n/a	n/a	n/a	1200	n/a	79.9	2	2016	Japan	[111]
GR + VPSA	OBFG	n/a	n/a	n/a	906–1117	1313	n/a	2	2016	China	[128]
GR + VPSA	OBFG	n/a	n/a	n/a	607	n/a	79.9	2	2015	India	[110]
GR + VPSA	BFG	n/a	n/a	n/a	n/a	n/a	n/a	6	2009	Sweden	[169]
.3. Pre combus	stion CC with memb	oranes									
2-stage memb.	BFG	n/a	n/a	32.5-50.6	n/a	n/a	90–98	2	2018	France	[162]
GR + 2-stage memb.	BFG	n/a	1.0 <sup>a)</sup>	34.4 <sup>a)</sup>	842	1268	95	2	2018	Korea	[160]
2-stage	BFG	n/a	n/a	32.5-50.6	n/a	n/a	n/a	2	2017	France	[173]
2-stage	BFG	n/a	0.9 <sup>a)</sup>	17.5 <sup>a)</sup>	407 t/h	420 t/h	90	3	2007	Norway	[174]
-stage	BOFG	n/a	n/a	n/a	n/a	n/a	55	4	2022	Korea	[175]
nembrane + cryogenic	BFG	n/a	1.6 <sup>a)</sup>	28.8 <sup>a)</sup>	n/a	n/a	97.1	2	2022	China	[178]

6.4. Pre combustion CC with SEWGS

#### Table 8 (continued)

Method/ Technology	Source	Thermal Penalty	Electrical Penalty	Cost	CO <sub>2</sub> emission reduction	Total CO <sub>2</sub> produced <sup>c)</sup>	CO <sub>2</sub> purity	TRL	Year	Country	Ref.
-	_	MJt/ kgCO <sub>2</sub>	MJe∕ kgCO₂	\$/tCO <sub>2</sub>	kgCO <sub>2</sub> /tHM	kgCO <sub>2</sub> /tHM	%	-	-	-	-
3.1. Post combustion CC with chemical absorption											
SEWGS WGS + SEWGS	BFG BFG, BOFG, COG	n/a n/a	n/a 1.9 <sup>a)</sup>	n/a 36.4 <sup>a)</sup>	14 t/day 759	n/a 2016	n/a 97.6–99.6	6 2	2018 2020	The Nether. Italy	[179] [32]
SEWGS w/ saturator	BFG, BOFG, COG	n/a	n/a	n/a	833	1422	n/a	2	2019	Romania	[45]
SEWGS w/ saturator	BFG, BOFG, COG	n/a	2.9 <sup>a)</sup>	n/a	149 g/kWhe	1339 g/ kWhe	98.85	2	2015	Italy	[29]
SEWGS + Ca- Cu	BFG, BOFG, COG	n/a	n/a	n/a	617	1922	96.8	2	2017	Spain	[93]

<sup>a)</sup> Electricity penalty and cost includes  $CO_2$  compression to 100–150 bar.

<sup>b)</sup> It is only accounted the decrease of  $CO_2$  because of injecting TGR and making oxy-blast furnace, and not the decrease that would be achieved by storing underground the pure  $CO_2$  from the CC stage.

<sup>c)</sup> Typical CO<sub>2</sub> emissions in an integrated steel plant are 1900–2200 kgCO<sub>2</sub>/tHM. When lower than this value, the total CO<sub>2</sub> produced in the industry refers to the steel plant without the power plant, or refers only to the blast furnace.

potential is represented in Fig. 18, where the space representing the rage of each KPI values in the reviewed works is highlighted for each category of technologies. The highest electricity penalty with lower  $CO_2$  emission reduction is obtained with oxy-TGR, but as noted above, the  $CO_2$ decrease depends on how it is measured, and the high electricity penalty is due to the high demand of pure oxygen (high ASU consumption). For post-chem, CaL, pre-chem and pre-adsor, three studies per technology were identified that analysed both KPIs. Post-chem and pre-adsor have a wide range of  $CO_2$  reduction while maintaining the electricity penalty at reasonable levels. CaL and pre-chem have less sparse range of values obtaining similar electricity penalty, with the former achieving higher  $CO_2$  emission reduction. Finally, the technologies with scarce data are pre-memb and SEWGS, while for post-memb, ChL and OtherL no scientific studies analysing both KPIs were identified, which highlights the necessity for further research in this field.

With the aim of highlighting the most studied or novel technologies, Fig. 19 shows the number of scientific papers organised by year and technology. Oxy-TGR is the most studied technology, with 30 published papers, with the first one from 2004. Other well studied and known technologies are post-chem, pre-chem and pre-adsor, with 22, 13 and 17 published papers, respectively, starting between 2007 and 2010. Among the most novel technologies, pre- and post-memb, SEWGS, CaL, ChL and OtherL can be found. Investigation of these novel technologies in the I&S industry began between 2014 and 2016, and therefore, none of them have more than 6 published papers.

For a rapid development of all CC technologies, the high costs and the availability of underground storage are the main bottlenecks. For new promising technologies, such as membranes, CaL or otherL, the low TRL and the lack of pilot plants can also be considered as a bottleneck, which slow down the development of these technologies. Besides, another technical limitation appears for pre-combustion CC technologies. These technologies capture CO<sub>2</sub> from energetic streams such as BFG, COG and BOFG, which also have significant amounts of CO and CH<sub>4</sub>. The two latter components will be combusted, converted to CO<sub>2</sub> and emitted to the atmosphere. This means that this pre-combustion technologies will never be able to capture all the CO<sub>2</sub>, and a significant amount of it will be released to the atmosphere. However, this problem can be partially solved if the CO is injected to the BF (i.e., TGR or hot reducing gases) as a reducing agent, as it will be oxidised to CO<sub>2</sub> and captured from the BFG in the pre-combustion CC stage. This partial solution is limited by the amount of CO that can be injected in the BF. Other possible solution to this problem is implementing a water gas shift (WGS) prior the pre-combustion CC stage, shifting all the CO to CO<sub>2</sub> and generating additional H<sub>2</sub>. However, this solution arises other economic and technical limitations regarding the use of pure H<sub>2</sub>, such as different combustion behaviour, high volatility, and higher compression energy.

#### 8. Conclusions

In this article, we have presented the first systematic review of the state of the art related to carbon capture (CC) technologies investigated to date for the blast furnace-basic oxygen furnace route of the I&S industry, in terms of energy penalisation, economic cost, efficiency, TRL and volume of  $CO_2$  captured. These technologies can capture  $CO_2$  from different streams, producing a concentrated stream of  $CO_2$  that can subsequently be stored or used.

Based on a systematic review procedure, 120 research articles were identified and reviewed. The reported carbon capture technologies were classified into four different groups: post-combustion, looping cycles, oxy-combustion and pre-combustion. Each group of technologies was further divided according to the specific CC technology applied: chemical absorption, physical adsorption, membranes, calcium looping, chemical looping and sorption enhanced water gas shift (SEWGS). For oxy-combustion CC technology, only oxy-blast furnace technology was found to be reported (i.e. oxy-combustion of BOFG or other gases were not found in literature, in relation to CC technology). When the capture is allocated in streams with combustible species such as BFG, BOFG or COG, it is considered a pre-combustion system, while when applied to flue gases, it is a post-combustion system. No study related to precombustion CC systems was identified for the solid fuels employed in the I&S industry (i.e., coal and coke).

An in-depth review of each carbon capture (CC) technology was carried out individually, as well as a detailed comparison of the technologies considering 6 KPIs: thermal penalty (MJ/kgCO<sub>2</sub>), electrical penalty (MJ/kgCO<sub>2</sub>), economic cost ( $\frac{1}{CO_2}$ , CO<sub>2</sub> emission reduction (kg/tHM), CO<sub>2</sub> purity (%) and TRL.

Calcium looping (CaL), precombustion CC by adsorption (pre-adsor) and postcombustion CC by chemical absorption (post-chem) are the three technologies that have lower electricity penalty when capturing high amounts of CO<sub>2</sub>. CaL technology achieves the highest CO<sub>2</sub> emission reduction at a lower cost, but other technologies such as post-chem, other looping processes (otherL) and pre-adsor achieve similar carbon capture rates. Precombustion CC by membranes (pre-memb) has the lowest economic costs, but with lower potential of carbon capture to date.

None of the technologies investigated for carbon capture are yet commercially available in the I&S industry, but some have achieved TRL 6, including postcombustion CC by membranes (post-memb), oxy-blast furnace with top gas recycling (oxy-TGR), precombustion CC by chemical absorption (pre-chem), pre-adsor and sorption enhanced water gas shift (SEWGS). The latter stands out as a promising alternative because, despite its high penalty, it has a low cost and very high CO<sub>2</sub> purity.

In the I&S industry, as the main  $CO_2$  streams have a similar  $CO_2$  content (i.e., 15–28 %vol) and a similar pressure (atmospheric to 2 bar), it is not of significant importance where the CC stage is implemented, the capture will behave similarly. Taking into account the 6 KPIs analysed, pre-adsor is found to be the most promising technology for capturing  $CO_2$  in the I&S industry, according to its high TRL and  $CO_2$  emission reduction at reasonable cost and penalty. The only drawback of this technology is the level of  $CO_2$  purity (88 % on an average), that is lower than for other technologies.

There are substantial opportunities for further investigation to characterise the actual potential of those technologies for decarbonisation of the I&S industry. Future research must reaffirm technologies with demonstrated positive outcomes such as pre-adsor, and also focus on new promising technologies such as membranes, CaL or otherL. Furthermore, the currently high costs of this kind of systems must be tackled, and there is a necessity to optimize the thermal and electrical penalties associated with carbon capture.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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#### Annex A. Main KPIs for reviewed CC technologies

The KPI data (i.e., thermal and electrical penalties (MJ/kgCO<sub>2</sub>), economic cost (\$/tCO<sub>2</sub>), CO<sub>2</sub> emission reduction (kgCO<sub>2</sub>/tHM), CO<sub>2</sub> purity (%) and TRL) extracted from the 120 studies reviewed and analysed in Section 7, is compiled in Table A for each technology, namely post combustion CC with either chemical absorption or membranes, Looping CC with calcium, chemical or other looping process, CC with oxy-blast furnace and TGR, and pre combustion CC with either chemical absorption, adsorption, membranes or SEWGS.

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