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# Current status of CO<sub>2</sub> chemical absorption research applied to CCS: Towards full deployment at industrial scale

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### Abstract

This work provides a wide overview of the state-of-art of the CO<sub>2</sub> chemical absorption applied to Carbon Capture and Storage (CCS) technology. The objective is not only to provide the current status of the technology and the research and development activities carried out towards its deployment in the CCS field, but also to identify the future directions and knowledge gaps. A summary of the conventional solvents used for acid gas removal and novel solvent formulations specifically adapted to new challenges such as fossil-fuels power plants and industrial processes was reported. Novel configurations from the conventional CO2 absorption-desorption layout were summarized and their impact on the operational performance and the reboiler duty was further evaluated. Novel opportunities offered by CO<sub>2</sub> concentrated flue gas derived from partial oxycombustion were further discussed in the final section. A large review of the published data from pilot plants has been done to facilitate the final comparison between the current status of postcombustion and novel partial oxy-combustion configurations. Demonstration plants currently available and the commercial solutions proposed by the most important companies were briefly described. CCS pilot plant via chemical absorption have been executed in last decades reaching several CO<sub>2</sub> capture capacities up to 80 t CO<sub>2</sub>/day. Commercial scale plants have been recently developed, being US and China the countries which lead the investment funds. The most important commercial scale demo plants, namely Boundary Dam and Petra Nova, were also described. Nevertheless, there were still many countries which need to bet for CCS at large scale.

# Keywords:

Absorption; Carbon Capture and Storage; CO<sub>2</sub> capture; Post-combustion; Partial oxy-combustion

# 1. Introduction

Climate change mitigation actions supported by the Conference of Parties (COP-21) is focused on holding a global temperature rise below 2°C and even further 1.5°C above pre-industrial levels by 2100. In this sense, the European Union (EU) has proposed the EU 2030 framework for climate change in which different mechanisms and policies to address climate change challenges are identified, laying down the groundwork of the European path towards decarbonisation by 2030 and beyond. The commitment consisted of four key pillars: reduction by 40% of anthropogenic greenhouse gas (GHG) emissions, 32% increase of the share of renewables in the energy supply network, 32.5% of improvements on energy efficiency, a 15% interconnection level of the internal energy market [1]. According to the IEA, global energy demand will grow by 25% by 2040, supported by an equal share of energy supply for oil, gas, coal and low-carbon sources [2]. Energy policies proposed by the EU council and economic growth in Europe will provide a 75% share of fossil fuels in primary energy demand during this period. The reduction in fossil-fuel dependence would not be enough to mitigate energy-related GHG emissions, showing a growth of 20% by this time. This outlook would produce a long-term global average temperature increase of 3.6°C, which is inconsistent with the IPPC 2°C-below target [2]. Therefore, the EU adopted the Strategic Energy Technology (SET) for smart, sustainable and adequate growth, in which the energy and climate challenges have been included [3]. This new energy policy aimed to address the transition to low carbon energy system based on several key challenges: energy efficiency, sustainable transport, security of supply, a smart and sustainable energy system [4]. R&ID activities should strengthen the large-scale renewable deployment and the strengthening of security as regards nuclear energy were pointed out to achieve the goal of two-thirds of electricity from low-carbon sources [5]. The SET Plan considers that carbon capture and storage (CCS) and utilization (CCU)

technologies plays a key role in in the portfolio of  $CO_2$  emission mitigation alternatives, but efforts must be made to address the barriers hindering its commercial scale development: energyintensive technology, reduction of overall efficiency in power plants or industrial processes, high operation and investment costs, lack of  $CO_2$  transport infrastructure in Europe, long-term  $CO_2$ storage safety, public acceptance, regulatory framework and  $CO_2$  pricing [6].

Within CCS alternatives, post-combustion capture using amine-based chemical absorption is a mature technology which can be ready to retrofit existing power plants in short-term [7]. For this reason, the CCS roadmap proposed by the SET Plan expects that the first commercial coal-fired power plant combined with CCS will be available in the period 2020-2025 and will be widely used in the rest of carbon-intensive industrial processes after that [8]. The key milestone for CCS deployment is set at a total CCS cost reduction of 30%-40% by 2020. It assumes that CCS will contribute up to 30% of the total GHG emission reduction by 2050 and the installed capacity of this technology will grow from 3 GW in 2020 to 3–8 GW in 2030, 22–129 GW in 2040 and 50–250 GW in 2050 based on a carbon pricing environment during this period. The European Industry Initiatives on CCS have identified the most relevant challenges that must be addressed to achieve the full deployment of this technology on a commercial scale. These challenges are divided in technological issues (for instance evaluation fully integrated CCS on a large-scale or performance and process configuration optimization from learning-by-doing strategies) and future development (CO<sub>2</sub> capture cost reduction below 60-90 €/t CO<sub>2</sub> and further research on CO<sub>2</sub> transport and storage alternatives) [9,10].

There are numerous review papers about CCS in the literature. In particular, several works reported the mechanisms of different solvents applied in  $CO_2$  chemical absorption such as ionic liquid, alkanolamines and their blends [11]. Furthermore, other works identified the main constrains hindering the deployment of post-combustion capture based on chemical absorption. In this sense, an assessment of the main barriers for post-combustion  $CO_2$  capture processes was also proposed, with the evaluation of several process intensification technologies [12]. Modeling of  $CO_2$  capture via chemical absorption processes is one of the most relevant topic and its more

recent advances have been also recently reviewed [13]. Moreover, a review of patents of  $CO_2$  capture technology development have been analyzed in recent published works [14,15]. Finally, some of the pilot scale CCS projects were studied by Yan and Zhang [16]. Nevertheless, this work is focused on the current initiatives and main insights on  $CO_2$  post-combustion capture based on chemical absorption leading for its full deployment at large scale. This work covers the most important knowledge gaps in regards of  $CO_2$  capture by chemical absorption which has not been summarized in other review papers, listed as follows: the commercial development of different configurations for  $CO_2$  capture in fossil-fuel power plants, as well as the current initiatives towards large-scale deployment of this technology; and also the identification of the cutting-edge of novel applications for  $CO_2$  chemical absorption such as partial oxy-combustion. Therefore, a needing for closing the gap of knowledge will come up in a near future. This work arises to serve as a guide for those involved in formulating new strategies – developing the existing technologies for  $CO_2$  capture by means of chemical absorption.

Herein a critical description of the state-of-art regarding currently post-combustion CO<sub>2</sub> capture processes is addressed, both those that are commercially available and those presently being researched. A summary of the post-combustion CCS demonstration projects worldwide is also provided. Based on this overview of the current state of the technology available, the current status of the CO<sub>2</sub> chemical absorption for CCS applications is analyzed in terms of the main characterization properties of traditional and novel both solvents and blends, as well as on optimized and integrated configurations from the traditional CO<sub>2</sub> chemical absorption layout, which are susceptible to being applied in this CCS technology. This work concludes with a description of the cutting-edge advances of the technology such as partial oxy-combustion capture processes, allowing for an evaluation of the areas that research should focus in this field. To fulfill the points announced, this work embraces references from different timespan. The basis of CO<sub>2</sub> capture by means of chemical absorption was first established from the nineties to the beginning of the present century by outstanding authors from that date. Therefore, the more basically aspects of our work were covered directly with literature from this period. In addition, the latest technological developments reported in this work intend to update the most forefront advances in  $CO_2$  capture with chemical absorption systems. Accordingly, a wide range of different novel references have been studied with a lifespan covered from 2012 to date.

### 2. CO<sub>2</sub> solvents

The fact that real solvents exhibits a combination of desirable and undesirable properties presents new challenges in terms of research into solvents, which should aim to achieve further improvements in CCS based on chemical absorption. A summary of the most relevant solvent tested for CCS applications is described below. Most of the studies dedicated to solvent performance improvements are based on two main approaches as given in sections 2.2 and 2.3.

### 2.1 First generation

The first solvents tested in CCS came from the traditional gas treating process. The amines that have been proven to selectively absorb  $CO_2$  from a gas stream on a large scale belong to the alkanolamine family [17,18]. Triethanolamine (TEA), a tertiary amine, was the first commercial solvent that was used in the early purification gas units, followed by monoethanolamine (MEA) diethanolamine (DEA), a primary and a secondary amine, respectively. and methyldiethanolamine (MDEA) diglycolamine (tertiary), (DGA) (primary) and diisopropanolamine (DIPA) (secondary) were also proven to be applied in CO<sub>2</sub> separation processes [19]. In general, the CO<sub>2</sub>-amine reactivity of the above-mentioned solvents shows a linear behavior in terms of the kinetics and the energy requirement for solvent regeneration, mainly depending on the chemical structure of the amine [13]. Primary and secondary amines commonly react with CO<sub>2</sub> to form the carbamate ion [20]. However, tertiary amines hydrolyze CO<sub>2</sub> based on acidbase considerations [21,22]. The carbamate formation produces stronger CO<sub>2</sub>-amine bonds than those from hydrolysis mechanisms, which results in higher energy requirements for CO<sub>2</sub> release and thus for solvent regeneration [12,23]. Most primary amines have an enthalpy of  $CO_2$  solubility about 80-90 kJ/mol CO<sub>2</sub>, being slightly lower for secondary amines (70-75 kJ/mol CO<sub>2</sub>). However, tertiary amines can absorb CO<sub>2</sub> with a significant reduction of the enthalpy of CO<sub>2</sub> solubility, which is usually found over in the range 40-55 kJ/mol  $CO_2$  [24]. Primary and secondary amines provide higher  $CO_2$  absorption rates than tertiary amines due to the carbamate formation. These facts make the selection of a proper solvent come down to a trade-off between high performance during  $CO_2$  absorption and the cost of the solvent regeneration: solvents that react with  $CO_2$  via carbamate formation show faster kinetics that can lead to lower equipment size but require more energy for regeneration [25]. Opposite effects are observed from solvents that absorb  $CO_2$  via hydrolysis [26].

## 2.2 Second generation - Functionalized solvents

Functionalized solvents are formed by the addition of chemical groups to the traditional solvent to alter its molecular structure and geometry. This fact modifies the position and size of the active areas and alters the length and the strength of the bonds formed from the reactive species. Sartori and coworkers [27,28] were the first who proposed this different class of solvents. These solvents, namely sterically hindered amines, form weaker CO<sub>2</sub>-amine bonds than primary and secondary amines and thus decrease the energy associated with CO<sub>2</sub> release without a significant reduction of the CO<sub>2</sub> absorption rate. 2-amino-2-methyl-1-propanol (AMP), 1-8-p-menthanediamine (MDA) (primary) and 2-piperidine ethanol (PE) (secondary) are examples of sterically hindered amines typically used for CO<sub>2</sub> separation process [28,29].

### 2.3 Amine blends

This approach combines different amines in order to hybridize their overall performance. The combination of a lower performing solvent such as tertiary amines with higher performing solvents such as primary amines can result in a mixture showing overall absorption improvements compared to those from the individual solvent separately. This practice is commonly referred to as promoting a solvent. MDEA was the first amine combined with faster kinetics amines to enhance its CO<sub>2</sub> absorption rate [30]. MEA, piperazine (PZ) and DEA have typically been applied to promote the MDEA solvent performance. Since MDEA blends were first employed in gas purification processes, a high number of mixed solvents have been proposed. Other works proposed the use of high absorption rates solvents to enhance the reaction kinetic of fast solvents [31]. In particular, MEA showed half of the absorption rates than those provided by PZ due to its molecule structure which contains two amino

groups. For this reason, PZ has been used as a promoter of MEA aqueous solutions. The MEA/PZ blend resulted in a substantially enhancement of the kinetic of the  $CO_2$  absorption reaction only adding a 5wt% of PZ [26,32].

The appearance of the CCS concept strengthened the interest in solvent development and research at the end of the 90s, with the possibility of extending mature  $CO_2$  chemical absorption technology to a new area: carbon capture from stationary sources, i.e. fossil-fuel power plants. Further studies have been carried out to determine specifically novel solvents and blends that strengthened their performance under applications for CO<sub>2</sub> capture in fossil-fuel power plants via CO<sub>2</sub> chemical absorption [33,34]. In this sense, the most desirable solvent properties that can be suitable for CCS applications include: high CO<sub>2</sub> loading, fast kinetics, thermal and oxidative stability, along with decrease in energy requirement for regeneration, volatility, viscosity, corrosivity, toxicity, chemical reactivity with impurities and cost [35,36]. In this respect, the CO<sub>2</sub> separation process based on mixedsalt solvent emerges as innovative option instead of conventional amine-based solvents. This novel approach is based on the use of ammonia blended with potassium carbonate [37]. Both the ammonia and the potassium carbonate showed several advantages compared to conventional amine-based solvents. They have low environmental impact based on their low toxicity. They do not degrade under high temperature neither the presence of impurities such sulphur compounds, nitrogen oxides and oxygen. They also showed high CO<sub>2</sub> loading cyclic capacity and absorption kinetics close to primary amines. It should be noted that they can be stripped at higher temperatures than conventional aminebased solvents and hence they are able to reduce the energy requirements for both the stripping of  $CO_2$ and the  $CO_2$  compression. However, the huge cooling requirements for the flue gas and the washing stage of the cleaned  $CO_2$ -free exhaust gas constrain currently its deployment at large scale [37]. The presence of potassium carbonate in aqueous ammonia had benefits on the overall performance of the solvent blend. The addition of K<sub>2</sub>CO<sub>3</sub> reduced the ammonia slip carried in the cleaned exhaust gas. In addition, the heat of  $CO_2$  desorption and the mass transfer coefficient were lower under more  $K_2CO_3$ in the solution. Experiments performed by Lillia [38], demonstrated a diminishing of the heat of desorption at 120 °C, from 70 kJ/kmol CO<sub>2</sub> to 55 kJ/kmol CO<sub>2</sub>, as the K<sub>2</sub>CO<sub>3</sub> concentration varied

from 1 m to 2 m in 4 m of total concentration of solvent in aqueous solution. At the same conditions, the mass transfer coefficient experienced a 21% of reduction. Results from modelling reported a 44% of reduction of the reboiler duty as mixed-salt were used instead of Econoamine Fluor FG+, reaching a specific energy consumption up to 2 MJ per kg of CO<sub>2</sub> for removing 90% CO<sub>2</sub> from a 550-MW supercritical power plant [39].

Furthermore, efforts have been made to address the main operational issues related to amine-based solvents. The use of corrosion inhibitors decreases the rate of corrosion and allows to use less expensive stainless steel in the pipework and the process equipment. It should be noted that higher concentrated aqueous solvent (up to 40 wt% in some cases, i.e. MEA [19,40]) has been used in chemical absorption since corrosion inhibitors started over to be employed. Higher concentrated solvents allow for lower equipment size and smaller amounts of water are required for the solvent preparation. Energy consumption can also be reduced by decreased pumping requirements. Other additives such as buffers, anti-foam additives and oxidative degradation inhibitors have been used to avoid common operation issues associated with amine-based solvents and to improve solvent performance in terms of lower degradation products disposal and solvent make-up [41].

An elevate number of blends and solvents has been identified for CO<sub>2</sub> capture based on chemical absorption and many studies can be found in the literature. Table 1 reported a list of the most promising studied in recent years. Rochelle's group from the University of Texas have investigated more than 50 different solvents that can be suitable for use as CO<sub>2</sub> solvents for post-combustion capture technology. K<sub>2</sub>CO<sub>3</sub> blended with PZ showed a high performance as a solvent blend from this research group [42,43]. In this sense, others research groups has employed potassium carbonate has been also tested as potential CO<sub>2</sub> capture solvent [44,45]. PZ has also been blended with other solvents such as AMP [46,47]. This blend has shown a relevant performance in comparison with conventional MEA 30wt%, reducing the energy consumption of the solvent regeneration up to 10% of the baseline case. The reboiler duty was set at 3.15 GJ/t CO<sub>2</sub> and the AMP/PZ blend shows its best performance elevated flue gas flow rate due to the presence of PZ (Fig. 1) [48].



Fig. 1. Specific energy consumption of different test campaigns at Kaiserslautern pilot plant and CO<sub>2</sub> SEPPL pilot plant using MEA 30wt% and AMP/PZ blend. Adapted from [48].

There are several commercial solvents available licensed by companies such as Fluor Daniel Co, Shell Co., DOW, BASF and MHI that will be described in following sections. An extended description of the solvent currently under pilot plant evaluation and its most relevant results will be also discussed [49,50].

A novel alternative for traditional amine-based solvents has been proposed recently, referred to as ionic liquids [51]. The ionic liquids are organic salts and normally provides low volatility and high boiling points. Their main advantage is that they are able to absorb  $CO_2$  and other acid gases providing lower energy penalties for the regeneration step than conventional amine-based solvents [52,53]. In general, they consist of the combination of a large organic cation, i.e. imidazole, pyridine or phosphorus-derived cation with an inorganic anion such as chloride,  $CF_3SO_3^-$  or flour-derived anion and  $RCO_2^-$  organic anion [54]. Ionic liquids can be produced by synthetizing under numerous configurations that allow them to be designed for a specific application. Despite their promising capacities for  $CO_2$  capture applications, there are some drawbacks limiting their development at large scales. Ionic liquids in combination with  $CO_2$  has shown high viscosity derived in operating issues and mass-transfer limitations for absorbing  $CO_2$ . [55]. Their prize is also not competitive compared with conventional solvents [56]. Ionic liquids are more suitable for moderate to high pressure conditions.

Solvent	Abbreviation	Туре	<b>Research Institution</b>	Reference
Piperazine and Potassium carbonate	$PZ + K_2CO_3$	Diamine secondary	University of Texas	[43]
2-((2- aminoethyl)amino)ethanol	AEEA	Diamine Primary	Norwegian University of Science and Technology	[32]
2-amino-2-ethyl-1.3- propanediol	AEPD	Diamine Primary and Secondary	Korea Electric Power Research	[32]
N-methylmonoethanolamine	MMEA	Primary	Institute of Chemical Technology (India)	[57]
N-ethylmonoethanolamine	EMEA	Secondary	Institute of Chemical Technology (India) and University of Paderborn (Germany)	[57]
Piperazine; 2-amino-2-methyl- 1-propanol	PZ + AMP	Diamine secondary + Primary (sterically hindered amine)	CSIRO Energy Tech	[46]
1,2-ethanediamine; 2-amino-2- methyl-1-propanol	EDA + AMP	Diamine Primary + Primary (sterically hindered amine)	University of Kaiserslautern	[58–60]
Amino acid salts	-	-	University of Twente (TNO)	[32]
-	CASTORs	-	Institut Fraçais du Petrole (IFP)	[32,61]
dimethyl-monoethanolamine; 3-methylamino propylamine	DMMEA + MAPA	Tertiary + Secondary	Norwegian University of Science and Technology	[62,63]
N,N,N ,N,N- pentamethyldiethylenetriamine - diethylenetriamine	PMDETA + DETA	Tertiary + Secondary	Huaqiao University	[64]
Monoethylene glycol – monoethanolamine	MEG + MEA	Primary	University of Surrey - Norwegian University of Science and Technology	[65]
Monoethylene glycol - N,N- dyetilethanolamine	MEG + DEEA	Tertiary	University of Surrey - Norwegian University of Science and Technology	[65]
Amino-functionalized ionic liquids - triethylenetetramine L-lysine	AFIL + TETAH	-	Huaqiao University	[66]
Carbonic anhydrase promoted potassium carbonate	$CA + K_2CO_3$	-	University of Kentucky	[67]
Mixture of diethylenetriamine	DETA	Secondary	North China Electric Power University	[68]
3-dimethylaminopropylamine, 3-diethylaminopropylamine and 3- piperidinopropylamine	DMAPA + DEAPA + 3PDPA	Tertiary	Hunan University	[69]

Table 1. Promising solvents for CCS capture under investigation

# 2.4 Key energy aspect for CO<sub>2</sub> solvents

Solvent regeneration contributes with 50-80% of the energy requirements consumption in postcombustion capture based on chemical absorption [24,70]. The total heat associated to the solvent regeneration is determined as the sum of the heat of the water vaporization, the sensible heat and the heat required for the  $CO_2$  release from the  $CO_2$ -solvent bond [71–73]. The vapour pressure of the solvent is higher than that of water and therefore the solvent vapourisation heat is often neglected in comparison with the latent heat of water vapourisation [74].

The sensible heat consists of the energy required for the rich solvent leaving the absorber to achieve the stripper temperature, commonly assigned to  $120^{\circ}$ C [72,75]. It depends of the specific heat capacity of the solvent. The stripper temperature should produce the water vapourisation from the solvent solution. The elevated latent heat of water – higher than 90 kJ/mole CO<sub>2</sub> – is the major contributor of the energy required during the solvent regeneration stage and depends on the stripping pressure [24]. According to Oexmann and Rochelle [74], higher stripping pressure reduces the H<sub>2</sub>O(v)/CO<sub>2</sub> ratio and therefore the energy associated to the latent heat of water term. The stream is required to produce the CO<sub>2</sub> stripping during its way up the column. Once the regeneration temperature is reached, the chain bonding between CO<sub>2</sub> and the solvent degrades and the reverse reaction of the absorption reaction occurs. Therefore, the energy required for CO<sub>2</sub> desorption from the rich-loaded solvent exhibits a direct relationship with the heat of absorption: the heat that is being released in the exothermic reactions occurring in the absorber must be provided in the stripper to reverse the absorption process and to drive out the CO<sub>2</sub> [74]. In MEA-based chemical absorption, the absorption heat accounts for 50–60% of the reboiler duty [75,76].

Fig. 2 illustrates the relative reboiler heat duty under variations of the relative stripping pressure respect to two generic solvents: Solvent A represents a high heat of absorption solvent whereas solvent B represents a low heat of absorption solvent. The stripping pressure has impact on the overall performance of the solvent regeneration process. The variations on the absorption and the heat of vapourization of water. In general, solvents with high heat of absorption (type A) –

 $(\Delta H_{sol} - \Delta H_{vap}) > 0$  – decrease the reboiler heat duty at elevated pressures whereas solvents with low heat of absorption (type B) –  $(\Delta H_{sol} - \Delta H_{vap}) < 0$  – experienced the same trend but at low stripping pressures, as Fig. 2 reported [74,77,78]. Typically, solvents A represent fast kinetic solvents and solvents B represent slow kinetic solvents.



Fig. 2. Comparative study of the overall energy requirement for CO<sub>2</sub> desorption for two generic solvents: high enthalpy of absorption (Solvent A) and low enthalpy of absorption (Solvent B).

# Modified after [74]

The heat of absorption is determined using a differential calorimeter reactor (DCR). The DCR measurements relies on the isothermal method. Once the solvent is placed into the reactors and the equilibrium temperature is reached, a gas stream containing a known amount of  $CO_2$  is bubbled in the measurement reactor. Since the  $CO_2$  absorption is an exothermic reaction, the differential temperature between the measurement reactor and the reference reactor (the temperature difference (DT) curve) is recorded during the absorption process. Finally, the heat of absorption was measured by integrating the DT curve obtained after the solvent is saturated on

 $CO_2$  [24,75,76]. Other approach applied in the heat of absorption determinations utilizes the experimental data related to VLE equilibrium (CO<sub>2</sub> partial pressure versus CO<sub>2</sub> loading) for different solvents [79,80]. The heat of absorption is a key indicator of the absorption kinetic of a solvent. It is estimated using the Gibbs-Helmholtz equation. Solvents with elevated heat of absorption indicate a great appetence for reacting with CO<sub>2</sub>. This appetence decreases as the same trend as the heat of absorption. In general, primary amines provide elevate enthalpy of absorption (80-90 kJ/mole CO<sub>2</sub>) and therefore high CO<sub>2</sub> absorption kinetics. Scondary amines showed lower kinetics than primary amines and also lower heat of absorption – from 80-90 kJ/mole CO<sub>2</sub> to 70-75 kJ/mole CO<sub>2</sub>-. The same trend was observed in tertiary amines which provide extremely lower kinetic compared with primary and secondary amines and also the lowest heat of absorption – ranging 40-55 kJ/mole CO<sub>2</sub> [24,81].

The enthalpy of absorption depends on other operating parameters such as the absorption temperature and the  $CO_2$  loading [75]. The  $CO_2$  absorption reaction is exothermal this process enhances at lower temperatures. Respect to the  $CO_2$  loading, Figure 3 represents the heat absorption under variations of the solvent loading. The behavior of amine blends follows the same trends and also depend on the  $CO_2$  loading of the solvent (Fig. 3) [48].



# Fig. 3. Heat of the CO<sub>2</sub> absorption of AMP/PZ blend and MEA versus CO<sub>2</sub> loading. Modified after [48]

According to Lin [24,76] and Kim [24,76], the enthalpy of absorption increases when absorption temperature increases for any solvent. The difference between the enthalpy of absorption under conventional absorption conditions (40°C-50°C) and under stripping conditions (120°C) increases up to 30% in some cases [76]. Moreover, higher CO<sub>2</sub> loadings lead to lower heat of absorption, as shown in Fig. 4.

Nevertheless, the stripping pressure and the concentration of the amine into the solution have no impact on the heat of absorption. In respect to pressure, experimental data have been reported from atmospheric pressure up to 100 bar. These experiments confirm that higher pressure facilitates the absorption of  $CO_2$  since more  $CO_2$  may be dissolved at higher pressures, resulting in a higher absorption capacity of the solution, but the enthalpy of absorption remains constant.



Fig. 4. Enthalpy of CO<sub>2</sub> absorption for several solvents at different CO<sub>2</sub> loadings. Modified after

### 3. Novel configurations and process integration into fossil-fuels power plants

Numerous measures were tested in order to lead for further improvements of the  $CO_2$  chemical absorption units since the first installations were erected for acid gas processing. Absorption and desorption processes are strongly coupled. Therefore, the simultaneous optimization of the whole process is crucial to achieve a substantial reduction of the total  $CO_2$  capture cost. One of the most promising approaches that can increase the plant efficiency is the heat integration between the power plant and the  $CO_2$  capture unit [26,82].

Many modifications from this basic scheme for gas processing operations have been proposed to reduce the energy requirements for solvent regeneration or equipment costs. For example, turbines have been utilized in high and moderate pressure absorption units for energy recovery. In the absorption section, the use of several lean solvent feed inlets were proposed to reduce the absorber size and hence the investment costs reactors [19]. Kohl and Nielsen [19] proposed to primarily add lean solvents in the central section of the absorber where the bulk of CO<sub>2</sub> was absorbed. A minor portion of the lean amine was fed at the top of the column to absorb the remaining CO<sub>2</sub> in the flue gas and therefore a reduced absorber diameter were required reactors. A concurrent absorption unit before the absorber was also proposed. The rich amine was pumped through the concurrent absorber before being sent to the regeneration process. In this unit, the high CO<sub>2</sub> concentrated flue gas was kept in contact with the rich amine to enhance the CO<sub>2</sub> loading of the rich amine by means of a switch of the CO<sub>2</sub>-solvent equilibrium. Therefore, the increase of the solvent capacity leads to lower solvent flow and lower energy requirements in the desorption process [19].

Another modification was proposed which has an impact on the absorber performance. It consists of the installation of intercoolers between the absorber packed beds to reduce the temperature inside the absorber. This approach withdraws a portion of the energy released during the  $CO_2$ absorption due to the exothermal reaction, avoiding excessive temperatures in the absorber that can negatively affect the absorption of  $CO_2$ . The optimum location of the solvent extractions along the absorption column was reported by Thompson and King [19]. They located the point near the bottom of the column where half the absorption occurs above and the other half below this location reactors. Solvent intercooler has been widely used in novel pilot plants applied to post-combustion capture studies [83]. In addition, a water wash is often added to the demister at the top of the absorber to reduce the solvent losses due to both amine volatilization and cleaned gas droplet carrier.

The split-flow scheme is illustrated in Fig. 5. In this option, the rich amine from the absorber sump is split into two streams, which are introduced in different sections in the stripping column. The stream fed at the top of the column is partially stripped along its way down and then is extracted at the middle section of the stripper. The semi-lean amine is pumped into the absorber, being introduced near the bottom where the bulk of the absorption occurs. The second split stream is introduced in the down section of the stripper where further CO<sub>2</sub> desorption is produced [84]. Then, the lean amine is pumped from the bottom of the stripper to the top of the absorber to yield the absorption of the semi-cleaned gas from the semi-lean absorption section. The use of split flow or inter-stage absorber cooling was demonstrated to get some energy savings. For example, Stee [85] proposed this configuration in a pilot scale unit and obtained a reduction of 5% in reboiler heat duty.



# Fig. 5. Flow diagram of the split-flow modification. Modified after [19,86].

Several drawbacks have been identified in the literature. The investment cost of the CO<sub>2</sub> capture unit is appreciably higher due to the fact that the height of the stripper must be increased somewhat and the process is more complex [87]. Moreover, the split-flow requires two sets of separate piping systems, including double pumps, heat exchanges and coolers [88]. Dubois [88] evaluated the influence of the stripping pressure under this novel configuration using a MDEA/PZ blend. An increase of the stripping pressure lead to a decrease of 25% of the regeneration energy of the optimum L/G ratio as the pressure varied from 200 kPa to 600 kPa (Fig. 6).



Fig. 6. Evolution of the specific energy consumption for MDEA/PZ blends under variations of the stripping pressure. Modified after [88].

It should be also noted that measures producing improvements to plant efficiency can lead to further capture cost reductions, but if they introduce new investment and operating costs, the benefits related to efficiency can be offset [84]. Therefore, a trade-off between marginal benefits associated to higher plant efficiency and extra-costs related to novel integration concept implementation should be analyzed prior to making a final decision that affects the design of the  $CO_2$  capture unit [26]. Efforts have been focused to develop both novel configurations and ideas

for process integration [89-91]. There are also studies focused on the evaluation of the most promising proposals [92,93]. In respect to CO<sub>2</sub> absorption, a lot of work related to CO<sub>2</sub> absorption improvements is reported from the literature. Cosmos and Gaspar [94] focused on mass-transfer and hydraulic considerations to provide an improved design of the absorber, whereas Fourati [95,96] relies on hydraulic aspects such as liquid spreading and dispersion to enhance the gasliquid contact and so extend the absorption capacity of the solvent. The feasibility of CO<sub>2</sub> capture using pulverized columns have also been investigated [97–99]. The integration of a coal-fired power plant with Chilled Ammonia process, using an absorption refrigerator (AR) to provide the chilling load was tested [100]. They obtained that the efficiency penalties can be reduced from 13.23% to 9.82%. More research works have been presented employing ammonia as capturing agent. CO<sub>2</sub> capture efficiency achieved was 80-90% with 5-15% NH3 concentration [101,102]. Moreover, removal percentages higher than 95% of SO<sub>2</sub> were presented. Two different electrolyte models for  $CO_2$  capture by means of ammonia were studied and compared [103]. Extended UNIQUAC model presented better experimental data for larger ranges of temperature and pressure than e-NTRL model. Costs were analyzed both for ammonia and amine based technology, resulting in lower values for the first one (47.03 €/ton CO<sub>2</sub> versus 51.62 €/ton CO<sub>2</sub>). Chilled ammonia process was also studied, which consist on capturing  $CO_2$  with ammonia as solvent at low temperatures [104,105]. CO<sub>2</sub> capture obtained varied between 75 and 85%, with less energy consumption than previous solvents tested (2.6 GJ/ton CO<sub>2</sub>) [104,105].



Fig. 7. Schematic diagram of multiple alteration configuration. Modified after [86].

Regarding desorption aspects, many novel stripper approaches have been proposed. Thermomorphic biphasic solvent (TBS) combined with intensification methods is considered a promising alternative for solvent regeneration [82,106]. It is based on the use of a lipophilic amine that can be separated into two phases at low temperature ( $75^{\circ}C-80^{\circ}C$ ). The organic phase formed contains the regenerated lipophilic amine, which can be converted to a single phase by cooling at 40°C-50°C, and the aqueous phase is mainly composed of water and carbamate amine species [107]. According to Zhang [82], extractive regeneration using inert hydrophobic solvents can reduce the desorption temperature down to 40–70 °C and intensifies solvent recovery, releasing more than 90% of CO<sub>2</sub> using multiple-stage extraction. This alternative might decrease the reboiler duty up to 50% respect to MEA 30%wt. Note that a new CO<sub>2</sub> capture technology based on the TBS process, referred to as the Demixing Solvent process (DMX<sup>TM</sup>), has been developed by IFP Energies Nouvelles. This technology uses a demixing unit prior to thermal regeneration [108]. After passing through this unit, the lean organic phase is returned to the absorber, while the rich solvent is sent to strip [95]. Zhang [90] proposed a flash evaporation showing a high

performance of the stripping section. In recent years, the use of modeling combined with technoeconomic evaluations has been done in order to assess each novel proposal before its further study at experimental scale [109]. Dreillard [108] proposed to use the produced CO<sub>2</sub> at 6 bars which turn into subsequent economical savings. According to their study, considering an available steam at 21  $\epsilon$ /t, it would be possible to produce CO<sub>2</sub> from blast furnace gases at around 40  $\epsilon$ /t. Finally, the feasibility of the best alternatives relies on the pilot plant evaluation and later demonstration scale development prior to a fully commercial deployment of the optimum process [26]. More recently, Dubois [88] compared various configurations of the absorption-regeneration processes in cement plant flue gases. They concluded that the heat pump modifications lean vapor compression configuration and Rich vapor compression configuration LVC and RVC lead to 11-18% energy savings of the CO<sub>2</sub> capture process compared to the baseline case using MEA 30%wt. Fig. 7 represents one of the multiple alteration configurations for amine-based absorption. It based

on the combination of intercooling in the absorption section, lean amine flash and evaporation of the condensate in the stripper section.



Fig. 8. Schematic diagram of a double matrix stripper configuration. Modified after [77].

According to Ahn [77], this novel configuration reduced the reboiler duty up to 2.2 GJ/t CO<sub>2</sub> of the energy required for the MEA 30wt% regeneration. Oyenekan and Rochelle studied several configurations of the stripping section and numerous solvents such as KS-1<sup>TM</sup> and solvent blends using PZ. This study concludes that the combination of MEA-MDEA blend and the double matrix configuration reduced the energy consumption of the overall CO<sub>2</sub> capture process up to 22% compared with the conventional configuration using MEA 30wt% as a solvent (Fig. 8) [77]. In addition, PZ combined with the advance flash stripper provided a 10% reduction of the energy required by the reboiler duty, the compression and pumping works [110]. Recently Wang [91] used a novel configuration to direct non-aqueous gas stripping process and exploiting its potential for energy saving through experiments. At ambient pressure for the regeneration stage, they obtained for pentane, hexane and cyclohexane, optimal energy consumptions of 2.38, 2.86, and 3.16 GJ/t CO<sub>2</sub>, which are 38.8%, 26.5%, and 18.8% lower than that of the conventional process to regenerate solvents from CO<sub>2</sub>.

Regarding the CO<sub>2</sub> contained in flue gas from natural gas treatment, CO<sub>2</sub> capture by means of chemical absorption is roughly applicable due to the low percentage of CO<sub>2</sub> in the flue gas – around 3-5%v/v CO<sub>2</sub>. For this reason, its application in this kind of power plants is not feasible and this CO<sub>2</sub> chemical absorption is still expensive for gas natural, being needed more advances to make it affordable. However, to reduce the impact of the low percentage of CO<sub>2</sub> in the flue gas on the CO<sub>2</sub> capture costs, the current research in this field aimed at increasing the CO<sub>2</sub> concentration in the flue gas in order to enhance the CO<sub>2</sub> absorption performance and hence reduce the operational and investment costs. Some of the different strategies to increase CO<sub>2</sub> in natural gas flue gas are listed below [111–113].

- Exhaust gas recirculation: CO<sub>2</sub> concentration can be increase up to 6%. The main impact is that compressor inlet temperature increases and it need to be cooled to avoid soot formation.
- Evaporative gas turbines: it produces an increase in turbine mass flow, which can affect

the pressure ratio. Moreover, the CO<sub>2</sub> concentration maximum to achieve is 6%v/v CO<sub>2</sub>.

- Supplementary fuel combustion: the overall performance is reduced by several points.
   CO<sub>2</sub> concentration could be increased up to 6%v/v CO<sub>2</sub>.
- Sequential supplementary gas combustion: as in the previous point, the main impact is that the overall performance is clearly reduced. Nevertheless, CO<sub>2</sub> concentration can be increased up to 9%.
- Selective exhaust gas recirculation in parallel: the maximum CO<sub>2</sub> concentration achievable by means of this technology is 18-20%. Nevertheless, this technology need to be further investigated to study the potential problems associated with it implementation.
- Selective exhaust gas recirculation in series: as in the previous point, this technology is very promising since it is estimated that a 20% of CO<sub>2</sub> composition can be achieved in the flue gas. The compressor working inlet conditions would drastically change in this scenario, but more research is needed to check the impact on the overall performance.

Other novel initiatives consist of the use of membranes in combination with solvents for  $CO_2$  capture. Membranes have been widely utilized in industry for natural gas treatment [114]. They consist of semi-permeable barriers that allow selective separation of a gas component from a mixture based on the permeation velocity of each component through the membrane. The membrane can be considered as a filter for one or more gas components and produces a component-enriched permeate stream. The differential pressure between the feed side and the permeate side is the main driving force to promote component separation from the flue gas. Although membrane technology can be applied in postcombustion applications, it is more suitable for pre-combustion -  $CO_2$  separation from H<sub>2</sub> and natural gas - and oxy-combustion -  $O_2$  separation from air-.

Gas absorption membrane aims to enhance the gas component separation using higher differential pressure as a driving force along the membrane due to the use of a  $CO_2$  solvent in the permeate side. In this case, the membrane is combined with a liquid solvent, typically an amine, which can immediately remove  $CO_2$  from the flue gas.  $CO_2$  is firstly diffused into the membrane and then is

chemically absorbed by the use of a solvent in the permeate side. The high  $CO_2$  removal rates provide smaller contactor devices using this principle than those from simple gas separation membrane. Moreover, using a membrane prior to  $CO_2$  removal by chemical absorption reduces the volume of gas to be treated in the absorber column and consequently decrease the equipment size and the operating cost associated with the overall process [115]. The driving force along the membrane decreases as  $CO_2$  is diffused into the membranes. This phenomenon impacts on the flexibility of the process, limiting its application in post-combustion due to the poor CO<sub>2</sub> recovery and purity. Barbieri indicate that the use of membrane in  $CO_2$  separation from flue gas containing less than 20%  $CO_2$  are inefficient. Membrane also requires a cooling stage to ensure the gas stays at a temperature below 100°C as higher temperatures produce a further degradation of the membrane materials [116]. Despite the low energy requirements  $(0.5 - 6 \text{ MJ/kg CO}_2)$ , the low CO<sub>2</sub> removal capacity and the low purity of the CO<sub>2</sub> stream make its implementation difficult on a large scale. Moreover, membranes do not provide a high separation level, so multi-stage and recycle configuration must be implemented to achieve an affordable degree of  $CO_2$  separation. It seems that membrane technology cannot tackle the energy penalties related to CO<sub>2</sub> separation in the post-combustion capture process, but its combination with existing processes, such as absorption membrane separation, may reduce the penalties of the overall CO<sub>2</sub> capture process. Some promising alternatives such as facilitated transport membranes, mixed matrix membranes have been also proposed in the literature [117].

# 4. CO<sub>2</sub> capture testing at pilot plant scale

Acquiring data from pilot plant campaigns is crucial to establish a set of design criteria for a further scaling-up of CCS technology toward commercialization. Novel solvents and blends aimed at reducing energy requirements for solvent regeneration are currently testing at pilot plant scale prior to being involved in a demonstration scale evaluation. The aim of these new synthetized solvents is to achieve a variety of desirable properties that can lead to lower energy penalties associated with carbon capture and an optimal process integration. It should be noted that although most of the studies on novel solvent formulation are focused on lowering energy

penalties related to solvent regeneration, some tradeoffs exists that must be considered [26,74]. A variety of properties, including corrosiveness, degradation rates, by-products derived from degradation processes, environmental impact, manufacturing cost and operating variables such as cyclic capacity, solvent flow-rate and stripping conditions, should be taken into account to evaluate the overall benefits in a CO<sub>2</sub> capture. Table 2 summarized the pilot plants and large experimental installations developed in recent years for the deployment of CO<sub>2</sub> capture at industrial scale, mainly focused on developing novel solvents and blends for CO<sub>2</sub> chemical absorption applications. The solvents, the main operating condition ranges encountered during the test campaigns and the results available in the literature have been also added. Most relevant studies by institutions such as the University of Texas, CSIRO, KEPRI-MHI, the University of Stuttgart (CASTOR and CESAR projects) and companies such as BASF, DOW, ALSTOM, Fluor Daniel are reported. Results from the latest activities carried out at the Mongstad pilot plant are also included. The experimental installations reported in Table 2 showed a CO<sub>2</sub> capacity ranging between 0.1-1 t CO<sub>2</sub>/day (low capacity level) and 10-80 t CO<sub>2</sub>/day (high capacity level).

			DOWL +LOTOL(	- ·	DICELDIDE	FOULELLOB	** **	
Institution/Company/Organization -	KEPRI-MHI	KEPCO-MHI	DOW-ALSTOM	Babkock-Hitachi	BASF-LINDE	EON-FLUOR	IHI	RITE
Date	2013	2016	2015	2012	2011	2009	2014	2018
Reference	[118]	[119]	[120]	[121]	[122]	[123]	[124]	[125]
Absorber								_
Diameter (mm)	400	-	1100-1200	-	-	-	850	-
Packing structure	IMTP50	-	-	Ring-shape	-	-	-	-
Height (m)	23.5	-	20.7+24.3	-	-	-	15	-
Number and height (m) of packing beds	-	-	-	-	-	-	-	-
Washing section (m)	Yes (-)	-	Yes (-)	-	-	-	-	-
Flue gas (Nm <sup>3</sup> /h)	350	1750	2500-5000	1000	1550	19400	4000	-
[CO <sub>2</sub> ] (vol%)	15	14.1	10-12	11	14.2	13	14-15	20
CO <sub>2</sub> capture (%)	90	90	90	80-95	90	90	90	-
Solvent	MEA 30wt%	KS-1™	URCASOL <sup>TM</sup>	-	MEA 30wt%	Econoamine FG Plus <sup>sm</sup>	ISOL's	IPAE-based solvents
Solvent flow-rate (m <sup>3</sup> /h)	1300*	-	12-25	1.5-3	-	-	24	-
L/G Ratio	3.7	-	3.8-5.3	-	-	-	-	2.5-3
Temperature (°C)	40	-	36-45	40	40	-	-	40
Stripper								
Diameter (mm)	0.35	-	600	-	-	-	-	-
Packing structure	IMTP	-	-	Ring-shape	-	-	-	-
Height (m)	17	-	26	-	-	-	-	-
Number and height (m) of packing beds	-	-	-	-	-	-	-	-
$CO_2$ capture capacity (t/day)	2	10	25	-	7.2	67.2	20	1
Reboiler duty (GJ/t CO <sub>2</sub> )	3.92	3.0-3.4	2.3-2.4	-	3.5	-	2.5-2.6	3.1-3.3
Lean solvent (mol CO <sub>2</sub> /mol solvent)	-	-	-	-	-	-	-	-
Rich solvent (mol CO <sub>2</sub> /mol solvent)	-	-	-	-	-	-	-	-
Temperature (°C)	113.8	-	-	-	-	-	-	-
Operating pressure (bar)	1.5	-	-	-	1.75-1.9	-	-	-
Extra Info	Nanko Pilot	Matsushima Pilot - KM-CDR™ process	Advance Amine Process (AAD) - derived from South Charleston	-	RWE PS at Niederaussem	Coal-fired PP at Wilhelmshaven	Aioi Pilot	RITE #1 and #2

Table 2. Summary of pilot plants and experimental installations for CCS deployment and results available in the literature

Institution/Company/Organization	DONG Energy	MONGSTAD	CO2CR-CSIRO		Univ. Stuttgart and Kaiserslautern	
Date	2019	2017	2	017		2017
Reference	[126]	[40,127,128]	[129]	[46]	[59]	[58]
Absorber					•	
Diameter (mm)	1100	541	-	211	125	
Packing structure	ITMP50	Flexipac 2Y HC	-	Pall rings	Mellapak	250Y <sup>тм</sup> - ВХ 500 <sup>тм</sup>
Height (m)	-	62	-	0.94		4.2
Number and height (m) of packing beds	4x4.25	1x12 + 2x6	-	4x0.135		5x0.84
Washing section (m)	3	6	-	-		0.42
Flue gas (Nm <sup>3</sup> /h)	5000	30000-60000	-	110-130		30-110*
[CO <sub>2</sub> ] (vol%)	12	3.2-11	9-15	11-13		3-14
CO <sub>2</sub> capture (%)	90	60-95	80-98	80-85	50-75	90
Solvent	MEA 30wt% and CASTOR 1. 2	MEA 30-40wt%	MEA 30wt%	AMP 25wt%/PZ 5wt%	MEA 30wt%	AMP 28wt%/PZ 17wt% and EDA 32wt%
Solvent flow-rate (m <sup>3</sup> /h)	40	30-150	-	0.33-0.54		50-350*
L/G Ratio	1.5-4	0.5-2.5	-	3.1-5.6	2.8 0.45-3.5	
Temperature (°C)	47	20-50	55.2	40		45-50
Stripper						
Diameter (mm)	1100	1300-2200	-	161		125
Packing structure	ITMP50	Flexipac 2Y HC	-	Pall rings	Mellapak	250Y <sup>тм</sup> - ВХ 500 <sup>тм</sup>
Height (m)	-	60	-	0.69		2.5
Number and height (m) of packing beds	2x5	2x8	-	1x0.390		3x0.84
CO <sub>2</sub> capture capacity (t/day)	1	80-275	2.4	0.1-0.2		0.1-0.25
Reboiler duty (GJ/t CO <sub>2</sub> )	2.6-3.8	3.4-4.16	-	4.4-9.2	3.98-5.01	3-3.8
Lean solvent (mol CO <sub>2</sub> /mol solvent)	-	0.2-0.25	-	0.04-0.13	0.08-0.09	0.1-0.18
Rich solvent (mol CO <sub>2</sub> /mol solvent)	-	0.44-0.48	-	0.26-0.28	0.11-0.14	0.2-0.28
Temperature (°C)	-	118-119	-	110-115		120
Operating pressure (bar)	3	1.9-2.5	-	1.43-1.59		1-2.5
Extra Info	Esbjerg PS	Statoil, Gassnova, Aker, TCM DA	Huaneng Changchun Pilot	Loy Yang PS in Newcastle (AUS)		CESAR Project

Institution/Company/Organization	Univ. Stuttgart and Kaiserslautern		Univ. Texas	Univ. Bucharest	NTNU	Univ. Kentucky	Univ. Graz
Date	2018		2016	2007	2018	2017	2017
Reference	[71]	[60]	[43]	[72]	[63]	[130]	[129]
Absorber							
Diameter (mm)	125		430	-	150	100	-
Packing structure	Mellapak 250Y™ - BX 500™		Flexipac 1Y, AQ, IMTP 40	Raschig 4mm	Mellapak 250Y	Pall rings	Raschig SPak200-X
Height (m)	4.2		13.3	4	-	7.3	-
Number and height (m) of packing beds	5x0.8	4	2x3.05	-	4.36	3.25	4x3
Washing section (m)	0.42		-	-	-	-	2
Flue gas (Nm <sup>3</sup> /h)	30-110	)*	180-900	-	150	23.8	100
[CO <sub>2</sub> ] (vol%)	3-14		3-13	10.5-12.3	11-13	14	11-13
CO <sub>2</sub> capture (%)	54-79	-	84.5-99	90	-	67-71	90
Solvent	MDEA 25wt%/n- MPDA 15wt% and AMP 25wt%/n- MPDA 15wt%	MEA and AMP 27wt%/EDA 19wt%	PZ/K <sub>2</sub> CO <sub>3</sub>	MEA 30-40wt%	MEA 30wt% and MAPA/DMME A	CAER-B2	PZ 25-36.7wt%; EDA 32wt%; NaGly 15- 40wt% and PZ 11.4wt%/K <sub>2</sub> CO <sub>3</sub> 22 1wt%
Solvent flow-rate (m <sup>3</sup> /h)	50-350	)*	1.2-5.3	_	0.12-0.24	0.1	-
L/G Ratio	1-4.6	1.1-2.8	1.8-6.9	3.5	-	-	1-10
Temperature (°C)	45-50	)	40	30-50	40-50	30	40
Stripper							-
Diameter (mm)	125		430	-	100	100-200	
Packing structure	Mellapak 250Y™	и - ВХ 500™	Flexipac 1Y, AQ, IMTP 40	Raschig 4mm	Mellapak 250Y	Pall rings	Raschig SPak200-X
Height (m)	2.5		13.3	-	-	-	-
Number and height (m) of packing beds	3x0.8	4	-	-	3.89	-	2x4 + 1x2
CO <sub>2</sub> capture capacity (t/day)	0.1-0.2	25	-	-	0.3	-	-
Reboiler duty (GJ/t CO <sub>2</sub> )	3.2-5.1	3.4-3.7	-	3.1-3.3	3.6-3.8	4.15-5.52	3.1-5.4
Lean solvent (mol CO <sub>2</sub> /mol solvent)	0.1-0.18	0.1-0.2	0.43-0.53	0.42-0.44	0.28-0.36	0.25-0.35	-
Rich solvent (mol CO <sub>2</sub> /mol solvent)	0.2-0.3	0.2-0.4	-	0.52-0.59	0.36-0.44	0.40-0.51	-
Temperature (°C)	120		74-143	96	111-118	-	-
Operating pressure (bar)	1-2.5		1-1.8	2	-	5.1	2
Extra Info	CASTOR Project (BASF)	CESAR #3		CFBC with capture			CO2SEPPL process at EVN PS at Dürnrohr

Institution/Company/Organization	Pilot-scale	Jaworzno II Power	UNO MK 3
	Advanced Capture	Plant	
	Technology (PACT)		
Date	2018	2013	2017
Reference	[131]	[85]	[132]
Absorber			
Diameter (mm)	300	330	100
Packing structure	IMTP	SULZER Mellapack	Steel Pall ring
Height (m)	8	5	4.25
Number and height (m) of packing beds	-	-	3/0.8
Washing section (m)	-	-	-
Flue gas (Nm <sup>3</sup> /h)	210	292	24-30
[CO <sub>2</sub> ] (vol%)	5-10	13.5	10-25%
CO <sub>2</sub> capture (%)	90	75-89	20-35
Solvent	MEA 30wt%	MEA 30wt%	K <sub>2</sub> CO <sub>3</sub> 20-40wt%
Solvent flow-rate (m <sup>3</sup> /h)	400-721	800-1600	30*
L/G Ratio	1.7-2.4	3.9-5.8	3-5
Temperature (°C)	40	40-60	50
Stripper			
Diameter (mm)	-	510	100
Packing structure	-	SULZER Mellapack	Steel Pall ring
Height (m)		6	
Number and height (m) of packing beds	-	0	3/1
$CO_2$ capture capacity (t/day)		-	5/1
Reboiler duty (GI/t CO <sub>2</sub> )		3 77-4 36	_
Lean solvent (mol $CO_2/mol solvent$ )	_	0 28-0 38	_
Rich solvent (mol CO <sub>2</sub> /mol solvent)	_	0.20 0.50	_
Temperature (°C)	-	105-110	150
Operating pressure (bar)	-	1	1
Extra Info		Jaworzno II Power Plant	UNO MK 3

Moreover, the CO<sub>2</sub> concentration in the flue gas varies from 3vol% to 15vol%. Results from pilot plant campaigns are not found for higher CO<sub>2</sub> concentrations due to the fact that the reported range of CO<sub>2</sub> concentration in flue gas derived from conventional air-fired coal combustion power plants. Therefore, further investigations are needed for evaluating the CO<sub>2</sub> absorption performance of solvents under partial oxy-combustion conditions. Retrofitting of current pilot plant configurations would be needed to execute new tests at those conditions and to assess whether the results can be compared with those from conventional post-combustion capture conditions. Various solvents have been proposed instead of MEA, covering a wide set of properties that can lead to lowering energy requirement during CO<sub>2</sub> stripping. Potassium carbonate promoted with PZ has been studied by Rochelle's group at the University of Texas and the University of Melbourne, showing higher cyclic capacity and a high performance in comparison with MEA [43]. Other blends include AMP with favored kinetic solvents such as PZ, EDA and MPDA, which resulted in lower energy requirements.

The specific energy consumption associated with MEA regeneration is found between 3.5 - 4.2 GJ/t CO<sub>2</sub>. As seen in Table 2, this energy requirement for most of the solvents were determined into the window 3-4 GJ/t CO<sub>2</sub>. However, a few of solvent showed a regeneration requirements below 3 GJ/t CO<sub>2</sub>. URCASOL<sup>TM</sup>, under the license of DOW and ALSTOM, showed the energy requirement below 2.3 GJ/t CO<sub>2</sub>. It should be pointed out ALSTOM is primarily focused on the development of ammonia-based chemical absorption, namely Chilled Ammonia [133]. IHI also determined low values for the regeneration of its solvent, decreasing the reboiler duty up to 2.5-2.6 GJ/t CO<sub>2</sub>. These values were reported from test campaigns carried out at the Aioi pilot plant using ISOL solvents. A novel solvent was tested at the Ferrybridge Power Station pilot plant, namely CCPilot100+ capture plant. The RS-2<sup>TM</sup> solvent exhibited both high absorption performance and significantly lower energy requirements than MEA. In general, the reboiler duty mainly consists of the sum of three terms, namely sensible heat, desorption heat and vapourization heat. The heat of the condensate reflux is also taking into account for several authors [134]. Most of the studies evaluate the contribution of each term into the total reboiler duty which strongly



depends on the operating conditions and the process configuration proposed (Fig. 9) [134].

Fig. 9. Share of the reboiler duty contributors for the regeneration energy requirement under different configurations of the CO<sub>2</sub> separation process: (a) low CO<sub>2</sub> partial pressure, and (b) high CO<sub>2</sub> partial pressure. Modified after [134].

# 5. Current initiatives towards large-scale commercialization

As can be extracted from previous sections, post-combustion capture based on chemical absorption is a mature technology that can be ready for its large-scale deployment in power generation and in other energy-intensive industries that use fossil fuels in the mid-term. A lack of data from demonstration scale units must be addressed prior to scaling up for commercialization. CCS feasibility and viability can be only achieved with public funding and technical support from companies through a demonstration stage prior to industrial-scale CCS projects. This section summarizes the current status of the efforts and supporting actions for CCS demonstration projects worldwide, including the experimental installations aimed at developing large-scale CCS technology.

Currently, there are several companies which developed commercial chemical absorption processes specifically focused to capture of  $CO_2$  capture. Econoamine FG Plus<sup>TM</sup> process,

licensed by Fluor Co., employs MEA blends as solvent. This technology has achieved reductions of up to 30% of overall energy consumption of the  $CO_2$  capture process compared with the conventional MEA-based configurations [50]. Mitsubishi Heavy Industries (MHI) licensed KM-CDR<sup>TM</sup> process which is based on the use of an own sterically hindered solvent, namely KS-1, in combination with an optimized configuration from the conventional process. The application of this technology in a  $CO_2$  capture process from pulverized coal power plants reduced by 15% the consumption associated with the conventional configuration of the company, placing the specific consumption of capture in 3 GJ/t  $CO_2$  [135].

Finally, Shell Co. provides a novel  $CO_2$  capture process namely Shell Cansolv<sup>TM</sup>  $CO_2$  capture system which is a world leading amine-based  $CO_2$  capture technology. This technology is suitable to be used in a widely portfolio of industrial process such as energy production, refineries, mining and chemical industries. The most relevant benefits are listed below [136]:

- Lower regeneration energy and superior kinetics compared to conventional amines
- High loading capacity combined with ease of regeneration
- Improved resistance to oxidative and thermal degradation
- Advanced solvent and technology development

The CCS demonstration projects currently under operation, execution or evaluation worldwide are listed in Table 3. A total of 22 demo projects are primarily focused on power generation and the share of post, pre and oxy-combustion projects is 9, 10 and 3, respectively. Most of the projects use  $CO_2$  injections for EOR, whereas other projects provide an opportunity to assess the feasibility of long-term  $CO_2$  sequestration in both saline aquifer and dedicated geological formations. The United States and China are the leading countries in CCS development, with 7 and 5 demo CCS projects, respectively.

The annual  $CO_2$  capacity for storage ranges between 0.8 - 3.8 Mtpa. Don Valley is recognized as the largest  $CO_2$  capacity project, with 5 Mtpa. However, the SaskPower Boundary Dam project erected in Canada is the large commercial scale facility for  $CO_2$  capture applied to fossil-fuel power plant in the world. It combines a coal-fired power plant with post-combustion capture and CO<sub>2</sub> storage. The captured CO<sub>2</sub> is used for enhanced oil recovery (EOR) in the oil field named Weybun [136]. From 2014 to the date, the capture facility at Boundary Dam has been operating. It has experimented some difficulties which resulted from a number of design deficiencies and construction, as well as some other issues which needed to be tackled down. These issues were safety, reliability and efficiency and cost-effective operation. Many projects were carried out to solve these problems and the results have been improving in terms of CO<sub>2</sub> capture tonnes. From November 2015 to October 2016, this plant achieved to capture 800,000 tonnes of CO<sub>2</sub>. By March 2018, 2,000,000 tonnes of CO<sub>2</sub> were captured in agreement with the latest available data [137]. A recent work studied the differences between Boundary Dam and Petra Nova model by means of a sensitivity analysis of the main parameters (for example coal type, CO<sub>2</sub> sale price and plant size). As main conclusion it was obtained that Petra Nova model has several advantages over Boundary Dam for new coal-fired power plants [138]. Petra Nova capture plant was designed to capture 90% of CO<sub>2</sub> emissions from a 240 MW coal plant (1.4 million tons of CO<sub>2</sub> per year). It is the largest CO<sub>2</sub> capture retrofit at a coal plant [139].

Project	Lifecycle stage	Country	CO2 capacity (Mtpa)	Operation date	Capture type	Storage type
Boundary Dam	Operation	CANADA	1.00	2014	Post	EOR
Kemper County	Done	USA	3.00	2016	Pre	EOR
Petra Nova (NRG Energy Parish CCS Project)	Operation	USA	1.40	2016	Post	EOR
Don Valley	Establish	UNITED KINGDOM	5.00	2019	Pre	Geological storage
FutureGen 2.0	Failure	USA	1.10	2017	Оху	Geological and onshore saline formations
HECA	Establish	USA	2.70	2019	Pre	EOR
ROAD	Operation	NETHERLANDS	1.10	2017	Post	Geological and offshore depleted reservoir
Sinopec Shengli	Operation	CHINA	1.00	2017	Post	EOR

Table 3. Status of CCS large-scale projects [16,137–145].

Texas Clean Energy	Establish	USA	2.20	2019	Pre	EOR
White Rose	Establish	UNITED KINGDOM	2.00	2020-21	Оху	Geological storage and offshore saline formations
Peterhead	Establish	UNITED KINGDOM	1.00	2019	Post	Geological and offshore depleted reservoir
Sargas Texas Point Comfort	Establish	USA	0.80	2017	Post	EOR
Bow City	Establish	CANADA	1.00	2019	Post	EOR
C.GEN	Under evaluation	UNITED KINGDOM	2.50	2019	Pre	-
Caledonia Clean Energy	Under evaluation	UNITED KINGDOM	3.80	2022	Pre	Geological and offshore saline formations with EOR
Huaneng GreenGen	Under evaluation	CHINA	2.00	2020	Pre	EOR and geological (under review)
Korea-CCS 1	Under evaluation	KOREA	1.00	2018	Post	Geological and offshore
Korea-CCS 2	Under evaluation	KOREA	1.00	2020	Pre	Geological and offshore
Quintana South Heart	Cancelled	USA	2.10	2018	Pre	EOR
China Resources Power (Haifeng)	Establish	CHINA	1.00	2020	Post	Geological and offshore saline formations
Dongguan Taiyangzhou	Establish	CHINA	1.20	2019	Pre	Geological and offshore depleted reservoir
SRI's ammonia- based CO <sub>2</sub> capture	Establish	USA - NORWAY	0.1	2019	Post	-
Shanxi	Under definition	CHINA	2.00	2020	Оху	-

The complete deployment of CCS technologies will not be achieved without policies that establish a price on CO<sub>2</sub> emissions. Indeed, stakeholders have identified a lack of a clear first-movement advantage. Developing CCS at demonstration scale is a costly undertaking. Such efforts must lead to a worthy knowledge that can outweigh the cost associated with its generation [146]. Although CCS development can provide advantages that ensure safe investment facing the future regulatory framework, the uncertainties related to this regulatory framework increase the likelihood that CCS deployment will be compelled [147]. The deployment of CCS technology for climate change mitigation purposes will therefore require policy action. In accordance with Bennet and Heidug, several break points have been defined in order to determine key changes in current policies designed for three difference steps [147].

- Step 1. Generation of knowledge for different CCS technologies as a public asset. This knowledge would help to identify high-performance and potential low cost CCS technologies.
- Step 2. If CO<sub>2</sub> pricing remains below the carbon capture cost, investment in CCS projects must be promoted by means of decreasing the risk exposure of stakeholders that can unlock private investment in CCS projects for continued learning-by-doing.
- Step 3. Once the mature CCS technologies achieve complete deployment, public investment must be reduced. It will require actors to address externalised CO<sub>2</sub> costs through carbon tax.

In this respect, a carbon price or an adequate emissions trade system is generally considered the most efficient mechanisms to assess efforts on CCS deployment and reducing CO<sub>2</sub> emissions [148,149]. Various carbon tax regulations have recently been put in practice in several regions, such as Australia and the EU, without success. Australia enacted a carbon tax in 2012 that was repealed in July of 2014, whereas the European Emissions Trade System (EU ETS) established a carbon price that has not driven any changes in private capital investment [150]. This non-competitive price makes cheaper for companies to emit CO2 rather than building the facilities to capture it. According to Maccoy [148], a global carbon pricing tax mainly affects the most carbon intensive industries, whereas performance standards, proposed by the EPA and Canada, force stakeholders to select a low-carbon, and also most expensive, technology. In the case of energy production, the final choice of the lowest cost of fossil-fuel power plant depends not only on the capture cost, but also the fuel price and the overall technology performance and efficiency.

Another aspect which has an impact on CCS performance is the  $CO_2$  storage regulation. Such laws and regulations were first proposed by regions as Canada, Australia and the EU, including a CCS-specific regulatory framework, a variety of recommendations for future regulatory actions and the EU directive and its accompanying guidance documents. Uncertainties such as  $CO_2$  quality for storage, long-term liability, transfer of responsibility and the future price of allowance will all likely prove key features in the global CCS process [151,152].

### 6. A new approach for carbon capture: Partial oxy-combustion

The energy requirements associated to both the  $CO_2$  desorption stage and the  $O_2$  separation from air are constraining the industrial deployment of post-combustion and oxy-combustion as CCS technologies, respectively. In this respect, the energy requirement related to the carbon capture process should be as low as possible, 2 GJ/t CO<sub>2</sub> being the target to be achieved [153]. A new hybrid concept falling between the above-mentioned CCS technologies can lead to further reductions of the energy consumption of the overall CO<sub>2</sub> capture process. This novel approach combines a combustion of fossil-fuels using oxygen-enriched air and a CO<sub>2</sub> separation process via chemical absorption using a flue gas with elevated CO<sub>2</sub> concentration [154–157].

Partial oxy-combustion emerges as a promising CCS technology for fossil-fuel power plants. The significant reductions on the solvent regeneration stages might make  $CO_2$  chemical absorption competitive among other CCS technologies and hence address one of the most important issues hindering the deployment of  $CO_2$  chemical absorption for CCS applications.

Several works on partial oxy-fuel combustion are reported from the literature. Favre [153] evaluated the technical feasibility of this novel process using the minimal work of separation concept. It consists of the theoretical minimal separation energy in an ideal gaseous binary mixture. Minimal work of extraction and minimal work of concentration were also used. The separation of a component in a gaseous mixture strongly depends of the initial composition of the feed stream [153]. Energy requirements of CO<sub>2</sub> separation significantly increased when a more diluted feed stream is used. Based on this phenomena, Favre [153] proposed to relax the constraints regarding oxygen purity towards a moderate oxygen enrichment that reduces the energy consumption of the ASU and facilitates the CO<sub>2</sub> separation of a higher concentrated flue gas provided by an enriched-air combustion.

Favre [153] studied the generation of low-specified oxygen production via cryogenic and  $CO_2$  separation using membranes. The specific energy consumption of the hybrid proposal for  $CO_2$  capture was determined by the sum of the two aspect above-mentioned. Favre [153] found an operating optimum ranging between 0.5 and 0.6  $O_2$  molar fraction in the oxidizer that lead to a minimal theoretical separation work of the overall power plant combined with  $CO_2$  capture. It should be noted that, according to Favre it is possible to achieve a 35% reduction of the overall energy requirement based on the use of an oxygen-enriched air, typically 40-60%, combined with a  $CO_2$  separation process using membranes with a selectivity of 50 or more in  $CO_2/N_2$  mixtures.

Doukelis [154] worked on the technical and economic evaluation of the combination of a fossilfuel combustion using air and oxygen followed by a carbon capture via conventional solvent scrubbing, namely ECO-scrub. This work was focused on a retrofitting alternative for CO<sub>2</sub> postcombustion capture ready plants. Two coal-fired power plants were studied, a 330 MW<sub>e</sub> lignitefired power plant and a 600 MW<sub>e</sub> hard coal-fired power plant. Air was used during the combustion process and an ASU provided the amount of high purity oxygen required to complete the combustion. A conventional MEA-based chemical absorption was used for CO<sub>2</sub> capture. Doukelis [154] concluded that the energy consumption related to oxygen production and CO<sub>2</sub> separation were slightly lower in the retrofitted case in comparison with oxy-combustion and conventional post-combustion processes, respectively. The CO<sub>2</sub> concentration in the flue gas was increased from 16.3% in the air-fired case to 23.54% in the ECO-scrub case. This fact caused a reduction of the MEA flow-rate of about 15.4%. Nevertheless, oxy-combustion produced higher net electrical efficiency in both plants and thereby a lower total electricity generation cost per electric production. In addition, authors pointed out that this novel approach requires a further capital investment in comparison with both CCS processes separately [153].

Variations of the partial oxy-fuel combustion have been proposed in the literature. Huang [156] proposed the use of a CO<sub>2</sub> compression and purification process directly instead of a chemical absorption process to obtain a ready-for-storage CO<sub>2</sub> stream, whereas Zanganeh [155] used air as a primary stream to carry the coal towards the boiler and employed oxygen-enriched oxidizer as

secondary stream to avoid operational issues regarding high  $O_2$  concentrated coal carrier streams. These studies confirm partial oxy-fuel as a potential CCS technology for  $CO_2$  abatement in fossilfueled power generation [155].

More recently, a novel Power-to-Gas technology synergized oxy-combustion technique with biomass [158]. A 2 MW<sub>th</sub> district heating case study was analysed, concluding a raise of the global efficiency up to 78.7%. Hanak [159] proposed a techno-economic analysis of oxy-combustion coal-fired power plant with cryogenic oxygen storage, realizing that benefits of energy storage can only be available at low capital investment. In this case, Implementation of energy storage can improve the daily profit by 3.8-11.6%. Regarding chemical absorption in oxy-combustion operation, Vega [160] proposed a novel study of the oxidative degradation of a novel AMP/AEP blend. Lower degradation rates than MEA as well as less losses were found. Moreover, NH<sub>3</sub> emissions were decreased up to 70% under partial oxy-combustion conditions. In a later study, this research group proposed an experimental study on partial oxy-combustion technology in a bench-scale CO<sub>2</sub> capture unit, revealing very promising results. The specific energy consumption was reduced up to 4.74 GJ/t CO<sub>2</sub> using a 60vol%. CO<sub>2</sub> flue gas resulted in 57% reduction compared with post-combustion (Fig. 10) [161].



Fig. 10. Specific energy consumption versus L/G ratios for different CO<sub>2</sub> concentrated flue gas.
Black points: 15% CO<sub>2</sub>; Blue curves: 20% CO<sub>2</sub>; Orange curves: 40% CO<sub>2</sub>; Grey curves: 60% CO<sub>2</sub>; and Yellow curves: 60% CO<sub>2</sub> (fresh amines). Reproduced with permission from [161].

Further improvements of the overall CO<sub>2</sub> separation process under partial oxy-combustion were provided using a relaxing stripping operating conditions [162]. Vega [162] evaluated the stripping performance under variations of the stripping temperature, using a 60% CO<sub>2</sub> concentration in the flue gas. Experiments run at 117°C and 118°C provided lower reboiler duty than those experiments run at conventional stripping temperature for MEA 30wt% (120°C). The best case was found at 118°C which reduced the reboiler duty up to 4 GJ/t CO<sub>2</sub>. This value corresponded with an 11% lower than conventional operation at 120 °C – 4.55 GJ/t CO<sub>2</sub> [162]. Cau [162] presented a techno-economic analysis for a CO<sub>2</sub>-free coal-fired power generation by partial oxyfuel and post-combustion CO<sub>2</sub> capture. Their analysis proved that this hybrid approach is not feasible for new plants, since the lack of commercial experience will continue to involve a high financial risk.



Fig. 11. Specific energy consumption of MEA 30wt% for partial oxy-combustion experiments run at stripping temperatures. Reproduced with permission from [161].

Most of the techno-economic studies used a combination of air with high purity oxygen production which lead to lower benefits in comparison with the direct production of oxygenenriched air as unique comburent. Some advantages have been identified that strengthen this hybrid concept. The main potentialities that should be investigated in order to complete the evaluation of this approach as a real CCS alternative are listed below:

- Possibility of reducing energy requirements related to high purity oxygen production by means of a low constraint of oxygen purity: oxygen-enriched air production instead pure oxygen production.
- Possibility of using alternative oxygen production technologies such as membranes and adsorption approaches instead of cryogenics, which can lead to a further energy reduction
- Strong enhancement of the CO<sub>2</sub> absorption process that can promote the CO<sub>2</sub> separation from a higher CO<sub>2</sub> concentrated flue gas with lower investment than post-combustion absorption.

It is clear that research into the  $CO_2$  chemical absorption performance under the above-mentioned operating conditions, particularly in a high  $CO_2$  concentrated environment, is crucial for strengthening partial oxy-combustion as a CCS technology. An optimal design of the absorption unit from the advantages observed should be evaluated to explore the real options of this approach against post-combustion and oxy-combustion alternatives.

### 7. Conclusion and future directions

The future actions for  $CO_2$  emissions mitigation relies on a decarbonization of the energy system. In this respect, the energy perspective for the period 2020-2050 still requires the contribution of CCS technology to meet the reduction targets of the anthropogenic  $CO_2$  emissions derived from energy-intensive industries and energy production. The contribution of CCS technologies is foreseen up to 30% of the total greenhouse gas emission reduction by 2050 based on 30-40%  $CO_2$  capture cost reduction of this alternative. This fact will produce an important growth on the capacity installed of CCS which were increased from 3 GW in 2020 to 50–250 GW by 2050.

This study confirms that a range of solvents for CO<sub>2</sub> capture via chemical absorption is available. Furthermore, the current status of chemical absorption development and the activities carried out to overcome CO<sub>2</sub> environmental aspects have been addressed. Among the solvents under investigation which are prone to be promising in terms of capture efficiency and energy consumption, the following ones have stood out: piperazine and potassium carbonate investigated by the University of Texas; Piperazine; 2-amino-2-methyl-1-propanol investigated by CSIRO Energy Tech; and the amino acid salts proposed by the University of Twente. Moreover, amine blends seem to be the most promising option since it combines different amines in order to hybridize their overall performance.

Novel configurations and process integration into fossil-fuels power plants were also reviewed. In this sense, partial oxy-combustion should be highlighted since high decrease of the regeneration energy was achieved by his proposal – more than 25% from baseline case -. CO<sub>2</sub> capture testing at pilot plant scale were also analysed for sake of comparison. Most relevant studies by institutions such as the University of Texas, CSIRO, the University of Stuttgart (CASTOR and CESAR projects) and companies such as BASF, DOW, ALSTOM, Fluor Daniel were reported. The experimental installations reported in this section showed a CO<sub>2</sub> capacity ranging between 0.1-1 t CO<sub>2</sub>/day (low capacity level) and 10-80 t CO<sub>2</sub>/day. Commercial scale plants have been developed during the last year, being US and China the country which lead the investment funds in this sense. The most important commercial scale plants are Boundary Dam and Petra Nova. Additionally, partial oxy-combustion configurations were reviewed offering a high number of published data.

Future directions should be leaded to deeper studies at commercial scale in developing countries such as China or India, which supposed the majority of  $CO_2$  emissions. Novel amine blends can be obtained also from further lab-scale works with better properties to reduce even more the energy consumption in the regeneration stage. Furthermore, value-added product from  $CO_2$  flue gases could be obtained to reduce the economic performance of chemical absorption processes such as obtaining carbonates products. Nevertheless, this option only can be implemented in small-medium  $CO_2$  producers since the amount of final product could be launched into the market at a competitive price.

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