

Application of CO₂ Removal to Reduce Emissions in a Steel Plant

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The steel industry is one of the major contributors to CO₂ emissions due to its energy intensive processes. Steel plants operate by converting iron ore into steel through processes like the blast furnace method, resulting in substantial emissions, primarily from the combustion of fossil fuels and chemical reactions. In order to manage this challenge, Carbon Capture and Storage (CCS) technologies play a pivotal role in mitigating emissions. These technologies capture CO₂ at the source and prevent it from entering the atmosphere. This work takes into consideration a French steel plant, producing 6.6 million tons of steel annually, and aims at designing the process of chemical absorption with a 30 wt.% MonoEthanolAmine (MEA) aqueous solution by optimizing it to reduce the thermal requirement for regeneration. The parameters that have been optimized are the height of the absorption column, the lean loading, the height and the pressure of the regeneration column and the temperature of the solvent entering in the regeneration column. Then, an economic analysis and the comparison of this technology with another technology for the CO₂ removal, the polymeric membrane method, has been carried out in order to understand the pros and the cons also taking into account the CO₂ purity and the CO₂ recovery ratio that can be achieved with the two technologies.

1. Introduction

In the early 19th century, the world annual steel production had been only a few million tons. After the breakthrough of new technologies, converter processes, and open hearths, the production increased and exceeded 30 Mt in 1900 by reaching its record in 1979 with 749 Mt. The growth then stagnated due to economic crises and political changes until the turn of the millennium, when it reached 850 Mt in 2000 (Holappa, 2020). Since then, the steel production has doubled and the record has been reached in 2022 with 1,885 Mt (WSA, 2023). About 70% of global steel is produced through the Blast Furnace and Basic Oxygen Furnace method (BF+BOF), which is also responsible for 95% of global iron production (IEAGHG, 2013). The remaining 30% is produced via Direct Reduced Iron (DRI) method (Chang et al., 1993), where the steel or solid iron from a DRI process is melted by electric power in an Electric Arc Furnace (EAF) (Thompson and Si, 2014, Quader et al., 2016). Ironmaking is an extremely energy-intensive process, utilizing coal as the main primary energy source though the use of natural gas is increasing (Jampani et al., 2019) because of its being the cleaner fossil source (Pellegrini et al., 2015, Spatolisano et al., 2023) providing less environmental impact than other fossil fuels. It has been estimated that 7–9% of direct emissions from the global use of fossil fuels (WSA, 2020) are related to ironmaking. The specific emission has been estimated equal to 1.85 t of CO₂/t of steel, corresponding to 3.3 Gt CO₂ in a year for a steel production rate of 1.8 Gt/y (Holappa, 2020). Nowadays, several technologies are available to reduce process plant emissions, such as Carbon Capture, Utilization and Storage (CCUS), that have started to be considered also for processes producing biogenic CO₂, as in Waste-to-Energy (WtE) plants (Pellegrini et al., 2023, Moioli et al., 2024). One of the main techniques for capturing CO₂ is the chemical absorption with aqueous solution of amines (Pellegrini et al., 2020) that are characterized by a very high efficiency though the most commonly used amines are toxic and subjected to degradation. Alternative solvents to amines for chemical absorption are being studied and also technologies based on different operations are under consideration, as membranes. They are thought more environmentally friendly as for the operation,

though being subjected to plasticization at high temperatures and to insufficient thermal and chemical stability (Yeo et al., 2012).

In a steel plant, blast furnace gases are estimated to contain about 70% of the CO₂ emitted and are the most relevant for volumetric flowrate (Ramírez-Santos et al., 2017). Though there is in general an interest towards the energy transition from fossil fuels to renewables (Spatolisano and Pellegrini, 2021), the production of gases containing CO₂ is part of the steelmaking process. Previous works in the literature considered CCS applied to steelmaking plants (Goto et al., 2011, Hooye et al., 2013, Arasto et al., 2014), and a review on the integration of carbon capture technologies in the Blast Furnace and Basic Oxygen Furnace (BF-BOF) (Perpiñán et al., 2023) has been published last year. This work presents a detailed assessment of the process design of the chemical absorption with a 30% wt. MonoEthanolAmine (MEA) aqueous solution (already considered for the CO₂ removal from flue gases of power plants (Moioli and Pellegrini, 2020)), that was not found in the previously published papers and that aims at better understanding the main factors contributing to the economics of the process to remove the carbon dioxide present in the blast furnace gas. An optimization has been carried out together with an economic analysis and then the amine-based technology has been compared to the membrane technology.

2. Simulation of the chemical absorption process

The process design has performed by simulating the chemical absorption process with a 30 wt.% monoethanolamine (MEA) aqueous solution in Aspen Plus[®] V11 software with the ENRTL-RK model, modified with the PC-SAFT to describe the vapor phase (Gross and Sadowski, 2000), and by considering the columns as rate-base units.

The blast furnace gas has a flowrate of 550,000 Nm³/h at 1.05 bar and 35 °C with the composition presented in *Table 1*, as the one studied by Ramirez-Santos et al. (2017). This gaseous stream (FLUEGAS) is treated in an absorption column with the solvent stream (LEANIN) entering at 1.2 bar and 40 °C.

Table 1: Blast furnace gas composition (Ramírez-Santos et al., 2017)

Gas	Unit	FLUEGAS
CO ₂	[% mol]	21.59
CO	[% mol]	23.45
H ₂	[% mol]	3.65
N ₂	[% mol]	46.51
H ₂ O	[% mol]	4.20
Ar	[% mol]	0.6

The process for the CO₂ removal includes three packed columns (Sulzer Mellapak 250X), a process-process heat exchanger, a heat exchanger with cooling water and two pumps. The blast furnace gas is fed to the absorber in which is treated with the liquid stream of solvent in a counter current configuration. The purified gas leaving the absorber (*GASOUT*), enters the washing section in order to decrease the emissions of MEA. Make-up water is added to the washing section, in order to control the amine emissions. The CO₂-rich solution (*RICHOUT*) is pumped to a process-process heat exchanger that increases its temperature in order to favor the desorption. Then, the CO₂-rich solution at high temperature (*RICHIN*) is fed to a regeneration column to separate the absorbent and CO₂. The concentrated CO₂ (*CO2OUT*) gas leaves the system while the remaining CO₂-lean solution (*LEANOUT*) is partially cooled down in the process-process heat exchanger (*LEANOUTMT*), mixed with a make-up (*LEANINLP*), fed to another heat exchanger and finally it is ready to be recycled back to the absorber. *Figure 1* shows a schematic of the process.

3. Results and discussion

3.1 Design of the process

In order to investigate the influence of lean loading and packing height on the energy requirement, the packing height of the absorption column has been varied from 10 to 26 m and for each of these heights different values of the lean loading have been simulated. In the simulations the impurity of 0.6% Ar has been considered as 0.6% O₂, with no influence on the results. In order to reach the desired recovery ratio of CO₂, fixed to 90%, it is necessary to modify the flowrate of the solvent according to the actual value of the lean loading. At low lean loading, more energy is needed to strip the CO₂ from the solvent, although less solvent is circulated. At high lean loading, a greater solvent flowrate is required, so the energy to heat the solvent to the reboiler temperature

is the main contributor the reboiler heat duty (*Figure 2a*) and the Thermal Energy Requirement (TER) is characterized by a minimum, that varies with the height of packing in the absorber.

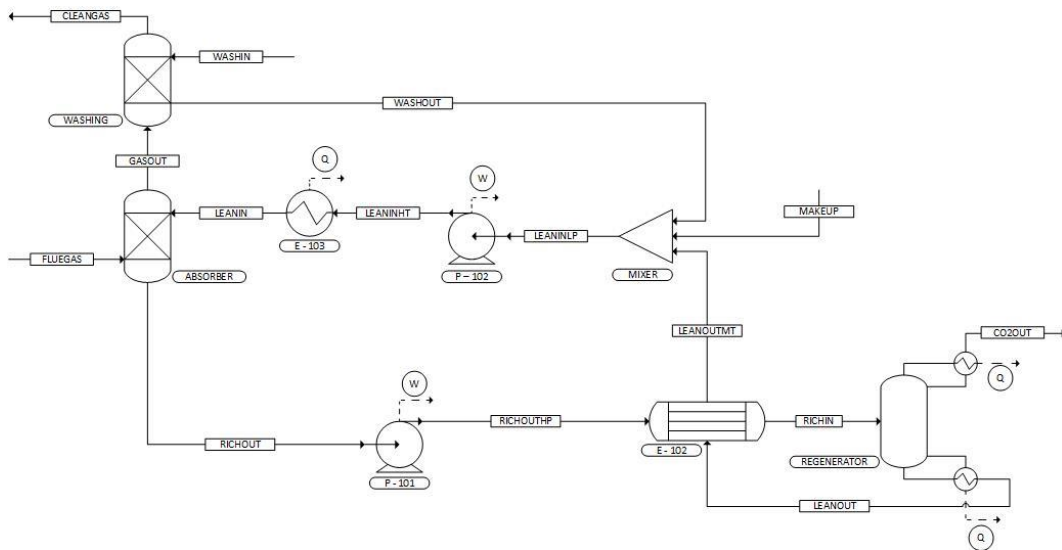


Figure 1: Process flow diagram of the MEA-based chemical absorption

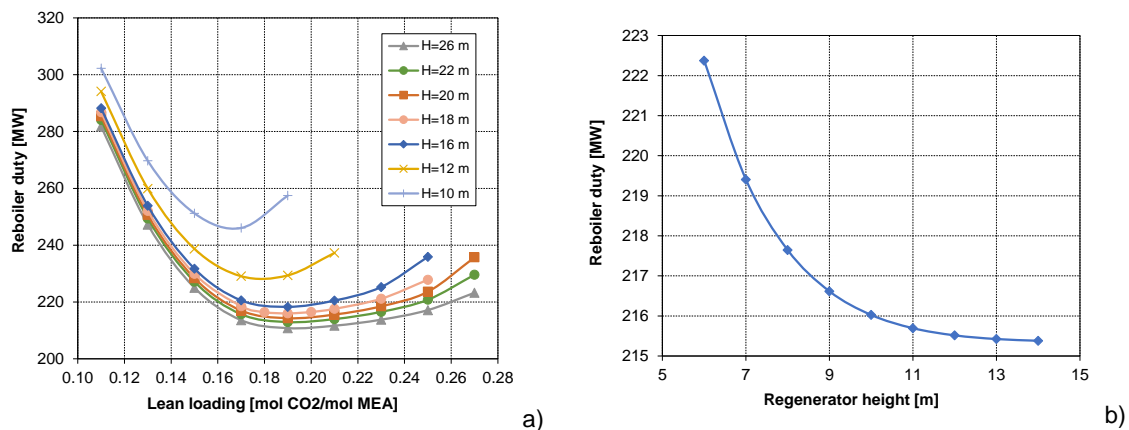


Figure 2: Variation of the reboiler duty with a) the absorber packing height and the lean loading and b) the packing height of the regeneration column

The objective of the regeneration column section is to regenerate the solvent and extract CO₂ from the rich solution by generating a vapour stream rich in water in the reboiler connected to the bottom of the column. For the optimum values of the absorber packing height and lean loading, the regeneration column packing height has been varied from 6 to 14 m. However, the reboiler duty increased significantly with lower packing heights (*Figure 2b*). So, 12 m is the optimal height that has been chosen for the regeneration column, because it is the first value that allows the reboiler duty to be nearly constant. Based on the process conditions reached after the optimization of regeneration column packing height, the regeneration column pressure has been varied in the range of 0.2 - 2.5 bar (absolute). All the other settings (absorber and regeneration column packing height, lean loading and absorber diameter) for the plant operation have been kept constant. As consequence of the variation of the regeneration column pressure, the mass flowrate of the absorbed CO₂ and thus the regeneration energy requirement change. Increasing the regeneration column pressure leads to a rise in the regeneration column temperature as can be seen in *Figure 3a* and the equilibrium isotherms of the CO₂ solubility shift to lower loadings at constant CO₂ partial pressure which means that the regeneration is easier and the regeneration is more effective with increasing the regeneration column pressure. Therefore, the reboiler duty for the solvent

regeneration decreases with a higher regeneration column pressure as can be seen in *Figure 3b* because less stripping steam is required for the separation task. The specific energy requirement to heat up the solvent flowrate is increasing with an increase in the regeneration column pressure because of the higher temperature at the reboiler. By considering the energy required by the reboiler, 1.8 bar has been chosen as the optimal pressure.

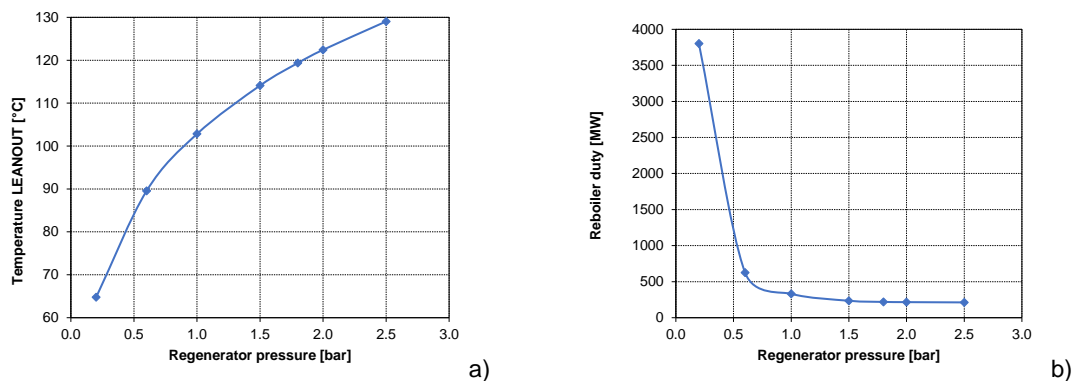


Figure 3: a) increase of the LEANOUT temperature as the regenerator pressure increases due to the different equilibrium conditions; b) decrease of the reboiler duty as regenerator pressure increases due to the less required stripping steam.

Based on the process conditions reached after the optimization of the pressure of the regeneration column, the solvent temperature has been varied in the range from 30 °C to 50 °C with all the other plant settings constant. In this study the influence of the solvent temperature on the reboiler duty has also been analyzed, though not reported here for reasons of space. As a result, the reboiler duty decreases as the solvent temperature increases because of the decrease in the amount of CO₂-rich solution that reaches the regenerator, which in turn is due to a greater vaporization of the water in the absorber. The optimized values for the process based on absorption are collected in *Table 2*. For these operating conditions, the absorption column operating at 1.02 bar is characterized by a temperature trend from 35 °C to a bulge and the regeneration column has a temperature profile from 30 °C at the top to 119.30 °C at the bottom.

Table 2: Design parameters of the optimized process

	Unit	Value
Absorber height	[m]	18
Lean loading	[-]	0.19
Regenerator height	[m]	12
Regenerator pressure	[bar]	1.8
Solvent temperature	[°C]	35

3.2 Economic analysis

The two main contributions to the plant total costs are the capital costs, related to the construction of a new chemical plant or modifications to an existing plant, and the operating costs involved in the daily operation of the plant. The Bare Module Cost accounts for both direct and indirect costs related to the project. Direct costs include the material needed for installation (piping, insulating material, structural support, etc.) and the cost of the equipment. Indirect costs include transport and insurance costs to the plant site with taxes, labour costs for installation and costs for engineering and supervision of the project. Also the estimation of the Cost of Manufacturing (COM) is required before the economic feasibility of a proposed process is assessed. There are many different factors affecting the cost of manufacturing a chemical product, that can be classified into three main categories being direct manufacturing costs, fixed manufacturing costs and general expenses. The Cost of Operating Labor is part of the COM. The computation of the operational expenses associated with a utility supply is performed by accounting only for the costs associated to the utility generation according to Turton et al. (2012) (Turton et al., 2012). The raw material used in this simulation are demi water and the solvent (MEA), with their costs estimated on the basis of the values excerpted from Moiola et al. (2019) (Moioli et al., 2019) and Mistral Industrial Chemicals (MIC). Moreover, large seasonal price fluctuations may exist for certain chemicals,

and therefore the average price over a period of several months should be considered in this case. Furthermore, the raw material cost includes the cost of solvent make-up due to losses and degradation. The investment costs related to the main units result to be equal to 25.39 M\$ for the absorber, 13.17 M\$ for the regeneration column, 8.67 M\$ for the heat exchangers and 0.82 M\$ for the pumps. The costs are annualized supposing a 25 year of life plant (Table 3).

Table 3: Total cost

Plant Total Cost	Unit	Value
Plant Life	[y]	25
Fixed Capital Investment (FCI)	[M\$]	96.07
Fixed Capital Investment	[M\$/y]	3.84
Cost Of Manufacturing (COM)	[M\$/y]	27.21
Total Cost during all the period	[M\$/y]	31.05
Cost of removed CO ₂	[\$/t CO ₂]	18.69
FCI per ton of removed CO ₂	[\$/t CO ₂]	2.31
COM per ton of removed CO ₂	[\$/t CO ₂]	16.38

3.3 Comparison with membrane technology

The main characteristics (CO₂ recovery, CO₂ purity in the CO₂-rich stream and total cost per ton of CO₂ removed) of the chemical absorption technology has been compared with the ones obtained with the polymeric membrane (Table 4) and presented by Ramirez-Santos et al. (2017). Differently from chemical absorption, the membrane technology is generally more suitable from bulk removal operations since the separation is based on a difference in a rate of permeation rather than on an absolute barrier to one component (Kohl and Nielsen, 1997). Though the chemical absorption has the disadvantage of using MEA as a solvent as it turns out to be corrosive and degrades at high temperatures and concentrations, this technology is less expensive and it is not characterized by modularity, favoring its application for high gaseous flowrates, like the one in the steel plant analyzed in this work. In the chemical absorption process the flowrate of solvent increases for a higher target CO₂ recovery (Moioli, 2023), with an increase of the costs, as in the case of the CO₂ removal process based on membranes. However, the CO₂ purity of the CO₂-rich stream exiting from the regeneration section does not vary, differently from the ones reported in (Table 4) for the membrane technology, that significantly decreases.

Table 4: Cost comparison

Technology	CO ₂ recovery [%]	CO ₂ purity [%]	Cost	Source
Chemical absorption	90	95	18.69 [\$/t CO ₂]	This work
Membrane	90	91.14	23.10 [€/t CO ₂]	Ramirez-Santos et al. (2017)
Membrane	95	87.91	25.70 [€/t CO ₂]	Ramirez-Santos et al. (2017)
Membrane	99	81.05	33.20 [€/t CO ₂]	Ramirez-Santos et al. (2017)

4. Conclusions

This work has focused on the study of CO₂ removal within the context of a steel plant. The utilization of chemical absorption, using MEA as the solvent, has been analyzed and optimized through simulation, offering insights into the performance and the economic viability of this technology. The parallel investigation, based on a case study of the same steel plant utilizing polymeric membranes for CO₂ removal, provides a valuable comparative perspective from which it is possible to outsource that, for the industrial plant considered in this work, the chemical absorption process can provide a reduction of greenhouses gas emissions at lower cost favoring the application of CO₂ removal to this type of production plants that emit relevant amounts of greenhouse gas. The future developments of this work could be the sensitivity analysis of the input variables and the study of CO₂ removal through an absorption process in which the solvent is more environmentally friendly than the MEA one.

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