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Abstract

In this paper we examine the feasibility and costs of recovering CO₂ from the flue gases for a conventional pulverized coal-fired power boiler using the concept of frosting and defrosting CO₂ at atmospheric pressure in a low-temperature evaporator.

The concept of frosting and defrosting CO₂ investigated is based on a 4-stage integrated cascade enabling the distillation of a refrigerant blend of 4 to 6 components; to evaporate the low temperature refrigerant fraction of the blend at temperatures varying between -90 down to -137°C (if necessary). The current design requires a swing process in the low temperature evaporators. The swing process allows to recover the sublimation and the melting CO₂ energy for temperatures varying between -120 and -56°C during the defrosting process.

In the first section, we describe how the process operates, the type of refrigerant blend used and how CO₂ is recovered in liquid phase at -56°C and 560 kPa.

In the second section, we describe the energy consumption and the energy efficiency of the total CO₂ capture process for the above-mentioned case study for a 90% CO₂ removal.

In the third section, the CO₂ frosting process is benchmarked with the conventional MEA-solvent based capture technologies.

1. Introduction

The Center for Energy and Processes at Ecole des Mines de Paris, in collaboration with ALSTOM, has developed a new technology for CO₂ capture. This technology is a tail-end treatment method based on CO₂ anti-sublimation at atmospheric pressure, which has been patented by ARMINES (Clodic and Younes, 2001, 2003a).

The capture scheme consists of anti-sublimating CO₂ on a low temperature surface (below -78.5°C), thus transforming the carbon dioxide directly from its gaseous phase into a solid phase frosted on the cold surface. Anti-sublimation allows CO₂ capture at a pressure slightly above atmospheric pressure therefore preventing any disturbance of the power unit operation.

2. Description of the CO₂ capture process by anti-sublimation

The process starts by cooling the flue gases from their initial temperature (around 60°C) down to the CO₂ frosting temperature (dependent on the CO₂ concentration as indicated in Table 1). The triple point of CO₂ is at 520 kPa, -56.6°C. At a pressure lower than the triple point pressure, CO₂ goes directly from the gas phase to the solid phase.

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Table 1: Frosting temperatures as a function of the CO₂ concentration in the flue gases*
(Clodic *et al.*, 2004b)

Concentration (%v/v)	100	10	1	0,1
Frosting temperature (°C)	- 78.5	- 103.1	- 121.9	- 136.7

* The saturating or sublimating temperature of a substance within a gas mixture depends on its partial pressure i.e. its corresponding concentration within the mixture

Cooling of the flue gases will continue until the corresponding exiting frosting temperature (around -120°C; depending on the desired capture efficiency) is reached. This change of frosting temperature is due to the decrease of the CO₂ concentration in the flue gases during capture. The CO₂ capture cycle is indicated on the CO₂ T-s diagram in Figure 1.

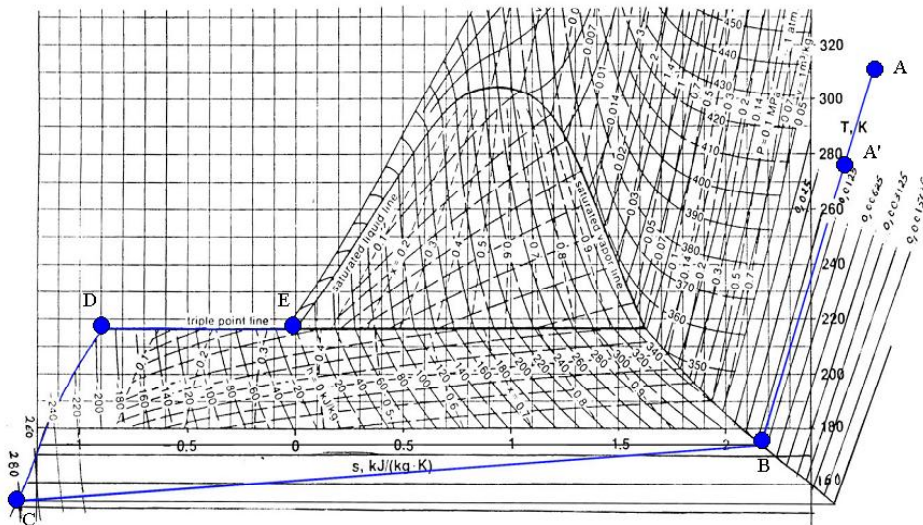


Fig. 1: Representation of the CO₂ capture cycle in the CO₂ T-s diagram (Younes, 2003b)

- Segment AB: represents the cooling of the CO₂ gas phase down to its frosting temperature
- Segment BC: represents the CO₂ frosting
- Segment CD: represents the CO₂ sublimation and temperature rise
- Segment DE: represents the fusion of the solid CO₂
- Finally segment CDE represents the recovered energy from the CO₂ coolness

The energy recovered from the CO₂ sublimation and fusion improves significantly the global energy efficiency of the process. This cold energy is recovered by the refrigerant blend circulating at a higher temperature inside the tubes of the frosted heat exchanger (around -45°C at the inlet) thus permitting the defrosting of the solid CO₂. The defrosting of the CO₂ is represented by segment CD (sublimation) and DE (melting) on Figure 1.

The frosting-defrosting process is performed alternatively in two evaporators, one frosting while the other defrosting as indicated on Figure 2.

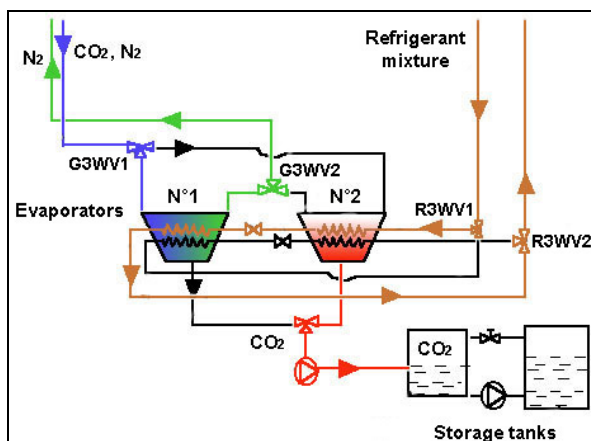


Fig. 2: Layout of the CO₂ capture system (Clodic and Younes, 2002)

Since the CO₂ freezing temperature is significantly lower than the water triple point characterized by a pressure of 0.6116 kPa and a temperature of 0.01°C, water has to be captured in the most efficient way, otherwise water vapor will freeze on the low temperature evaporators and thereby block the flue gases passage. Water capture is carried out at successive levels of temperature, first by condensation and then by a frosting/defrosting process to obtain dry flue gases proper for the CO₂ capture stage. The operational scheme of the CO₂ capture system by anti-sublimation is presented in Figure 3.

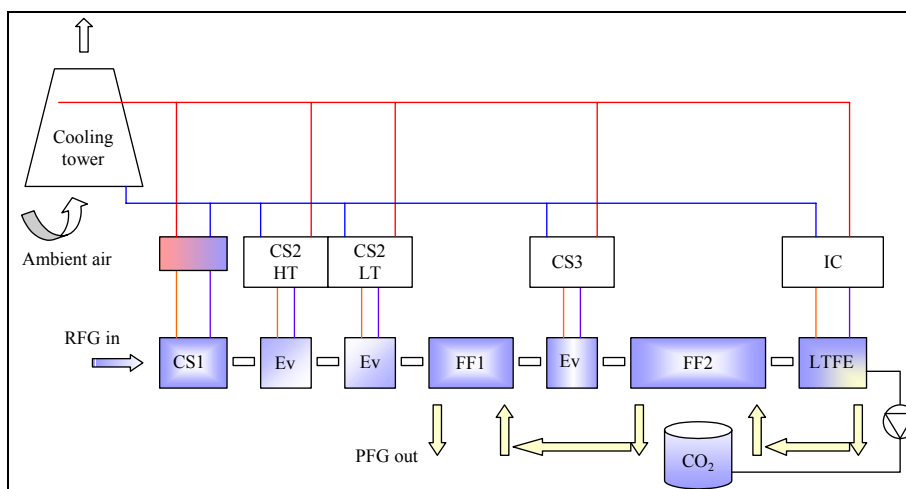


Fig. 3: CO₂ capture system operational scheme (Clodic *et al.*, 2004b)

The flue gases are first cooled to near ambient temperature by a first cooling stage (CS1) designated as the free cooling stage. The Flue Gases (FG) cooling is done by the ambient air and two water circuits (cooling tower). One circuit exchanging energy with the flue gases, while the other exchanging energy with the ambient air. A water/water heat exchanger links these two circuits together. This arrangement isolates the process water, which comes in direct contact with the flue gases, from any contact with the ambient air.

A second cooling stage (CS2) brings the flue gases down to 0°C. To achieve this temperature – under all ambient conditions – it was found that two successive levels of evaporating temperatures are most efficient with the lower being just above 0°C to avoid frost. It is necessary to achieve a 1.10^{-4} g H₂O/kg dryFG water content for the CO₂ capture stage. Flue gases at near 0°C have a 4 g H₂O/kg dryFG water content. Further drying would then be possible by either an adsorption or a frosting system. Calculations have shown that a frosting system is more energy efficient. The solution was retained for the third cooling stage (CS3). The frosting temperature chosen is around -40°C in order to design a classical simple refrigerating cycle and cut down the temperature decrease from 0°C to -121°C while achieving good flue gases drying; the water remaining in the flue gases at -40°C is about 0.08 g H₂O/kg dryFG.

A first heat exchanger (FF1) designed in counter current between the "Hot Flue Gases" (HFG) and the "Cold Flue Gases" (CFG) exiting the low temperature stage of the low temperature heat exchanger recovers more than 90% of the coldness of the CFG.

A second HFG/CFG counter current heat exchanger (FF2) is designed to operate between CS3 and the Low Temperature Frosting Evaporators (LTFE) in order to recover the coldness from the CFG leaving the LTFE. A special arrangement permits to frost and defrost the water content remaining in FF1 and FF2.

Finally CO₂ alternatively frosted on the heat exchanger fins of the LTFEs as indicated in Figure 2. The cooling capacity at about -120°C is delivered by the 4-stage Integrated Cascade (IC) described in Figure 4. The IC is a refrigerating system with only two levels of pressure (evaporating and condensing pressures) using a refrigerant blend of 4 to 6 components. The normal boiling points (NBP) of the components of the refrigerant blend are staged from the ambient temperature down to the lowest temperature level, i.e. for an integrated cascade to have an average evaporating temperature of -120°C, the blend can be made of n-butane (NBP -0.5°C), propane (NBP -42.2°C), ethane (NBP -88.6°C), and methane (NBP -161.4°C). So, at the same evaporating pressure, the higher NBP refrigerants are in a liquid state and are evaporated in order to partially or fully condense the lower NBP components.

The IC has to work all year round under different ambient conditions resulting in different condensing temperatures leading to adjustments in the circulating refrigerant composition to achieve a same evaporating temperature. A second option is to design the IC for winter conditions and set an additional Cascade Cooling Stage (CCS) to account for the temperature difference between summer and winter at the IC condenser.

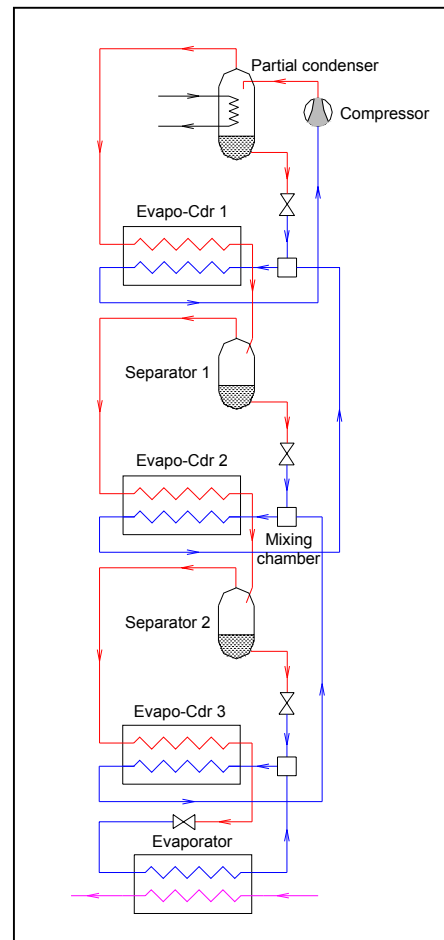


Fig. 4: The 4-stage integrated cascade (Younes, 2003b)

Experimental results

A first mock-up has been built and serie of tests have been performed in order to demonstrate the feasibility of the anti-sublimation CO₂ capture process and evaluate its efficiency.

Pictures 1 and 2 show respectively solid CO₂ frosted on the evaporator fins and liquid CO₂ defrosted and recovered in the evaporator enclosure.

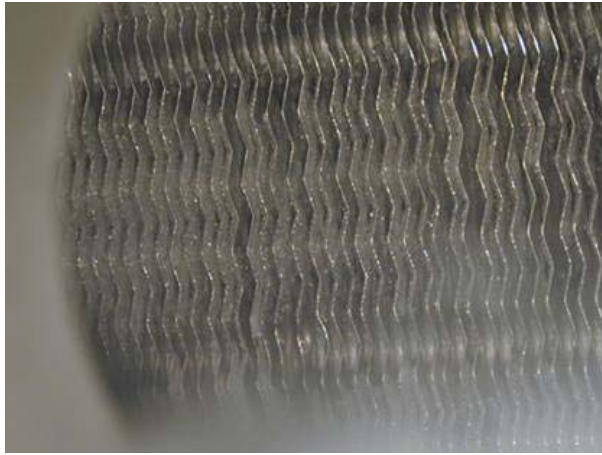


Photo 1. CO₂ frosting on the evaporator fins
(Clodic *et al.*, 2004a)

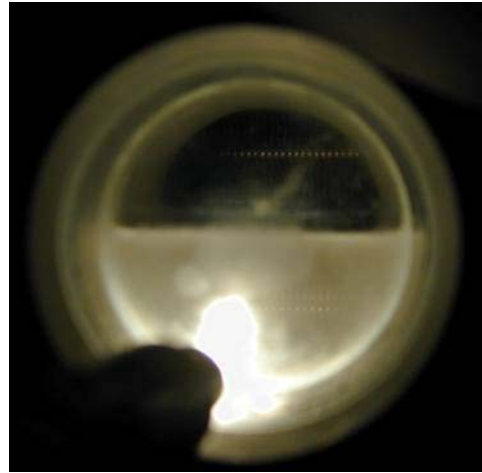


Photo 2. Liquid CO₂ after defrosting
(Clodic *et al.*, 2004a)

Figures 5 and 6 show respectively the CO₂ inlet and outlet concentrations as a function of time for inlet CO₂ concentrations of 3% and 13% respectively; a 90% CO₂ capture efficiency is achieved.

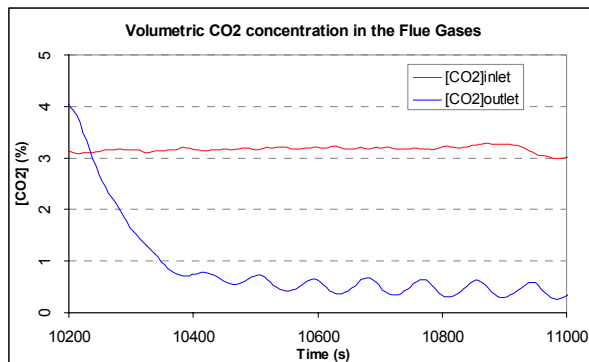


Fig 5 Evolution of the CO₂ concentration at the evaporator outlet for a 3% initial CO₂ concentration
(Younes *et al.*, 2005)

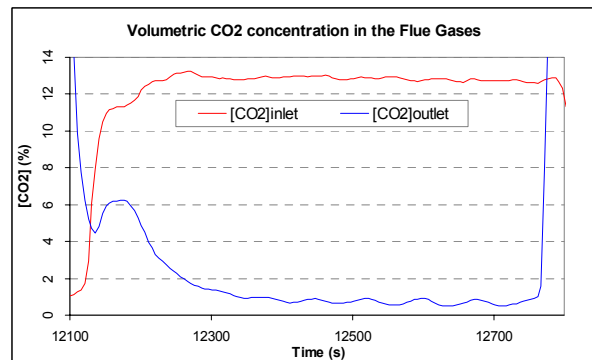


Fig 6 Evolution of the CO₂ concentration at the evaporator outlet for a 13% initial CO₂ concentration
(Younes *et al.*, 2005)

3. Energy consumption of the CO₂ capture process by anti-sublimation for a pulverized coal-fired boiler

The PC fired boiler flue gases composition that is considered for this study is given in Table 2 as well as their corresponding composition after water removal.

Table 2 Boiler flue gases composition (Clodic *et al.*, 2004b)

	N ₂	CO ₂	O ₂	H ₂ O
Initial composition				
%mass	68.92	15.47	6.75	8.86
% vol	70	10	6	14*
Composition after water removal				
%mass	75.62	16.97	7.41	0
% vol	81.39	11.63	6.98	0

*The high water content is due after-treatment systems typically used on a boiler flue gases

The flue gases leaving the boiler are considered at 60°C temperature and 120 kPa pressure. The ambient conditions for calculating the cooling capacities and power consumptions are considered at 15°C temperature, 60% relative humidity, and 101.3 kPa pressure, which gives a cooling water availability at the cooling tower exit of 15°C.

In order to evaluate the energy consumption related to the CO₂ capture process, all cooling systems and annexes have to be accounted for. The energy efficiency depends mainly on the global design, the compressor efficiency (commonly between 0.5 and 0.85) and the choice of the expansion components (expanders or expansion valves). Taking into account these different options, the refrigerating systems can be evaluated by their COPs (coefficients of performance), and more generally by the so-called

cycle efficiency η_{cycle} , defined by:

$$\eta_{\text{cycle}} = \frac{COP_{\text{actual}}}{COP_{\text{Carnot}}} \quad (1)$$

Knowing the evaporating and condensing temperatures for all the refrigeration cycles involved in the system, it is possible to express the achievable energy efficiency between two high and low thresholds. Table 3 gives the cooling capacity and the electrical power consumption for each refrigeration group of the system. The CO₂ capture efficiency is considered at 90%. The high and low COP values correspond to cycle efficiencies of 80 and 50% respectively.

For an initial CO₂ concentration of 10% v/v and a final concentration of 1% v/v, the total energy consumption varies between 647.7 and 1,248.6 kJ/kg CO₂ depending on the cooling system efficiency.

Table 3 Summary of the cooling and electrical energies needed for CO₂ capture by anti-sublimation (Clodic *et al.*, 2004b)

	Cooling energy needed by the FG (kJ/kg dFG)	Refrigerating system COP	Electrical energy (kJ/kg dFG)	Electrical energy (kJ/kg CO ₂)
CS1 from 50 to 23°C	256.76		5.13	30.3
CS2 HT from 23 to 13.5°C	25.58	High 19.7	1.3	7.6
		Low 12.3	2.1	12.3
CS2 LT from 13.5 to 3°C	21.14	High 9.9	2.1	12.6
		Low 6.2	3.4	20.1
Cooling to -40°C	21.26	High 2.8	7.9	46.4
		Low 1.75	12.5	73.7
Cooling to -120°C	120.7	High 0.91	132.6	781.6
		Low 0.57	211.7	1'247.8
Defrosting		High 0.91		- 254.8
		Low 0.57		- 159.6
Auxiliaries			4.1	24.0
Total		High		647.7
		Low		1,248.6

The total energy consumption depends on the CO₂ initial concentration in the flue gases as well as the desired CO₂ capture efficiency. This is so since the COP of the refrigeration system depends on its evaporating temperature, which is the result of the two constraints, cited above.

Figure 7 shows the evolution of the energy consumption as a function of the CO₂ concentration in the flue gases based on a 90% CO₂ capture efficiency and a 65% refrigeration cycle efficiency referred to Carnot. The water concentration is considered 10% v/v for all the calculations. It can be seen that the slope of the curve is sharp at low CO₂ concentrations while it smoothes at high concentrations. Thus, although anti-sublimation for CO₂ capture can be used at either low or high CO₂ concentration, the energy penalty is significantly lower for concentrations above 10%.

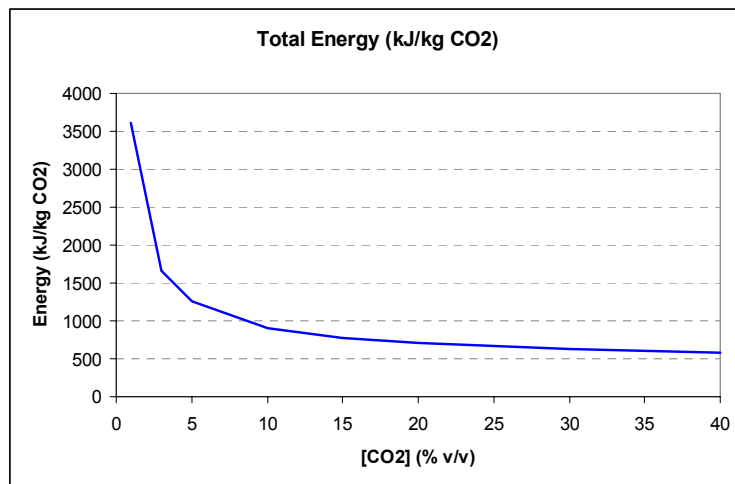


Fig. 7: Energy consumption function of the CO₂ concentration for a 90% CO₂ capture efficiency (Younes, 2003b)

4. Description of the CO₂ capture process by MEA for a pulverized coal-fired boiler

Monoethanolamine (MEA) is widely used and processes using it were developed in the 1940s for general, non-selective removal of acid gases, such as CO₂ and H₂S, from natural gas streams which are generally oxygen free. The process was modified to incorporate inhibitors to resist solvent degradation and equipment corrosion when applied to CO₂ capture from flue gases in which oxygen is present. These modified processes were developed to meet the needs of the merchant CO₂ market and latterly, at a much larger scale, for the production of CO₂ for enhanced oil recovery (EOR).



Picture 3: Absorber (foreground) and stripper (background)¹

¹ The CO₂ capture facility at the AES power plant Warrior Dun, Cumberland, USA. Courtesy of AES

A typical example of an amine scrubbing unit and process is shown in Picture 3 and Figure 8. The process allows flue gases to be quenched prior to contact with an MEA solution in an absorber. The MEA selectively absorbs the CO₂ and is then sent to a stripper in which the CO₂-rich MEA solution is heated to release the CO₂. The lean MEA solution is then recycled to the absorber. Commercially available processes contain additional features to achieve a high degree of thermal integration within the process in order to minimize the stripping heat load. All of the commercially available amine scrubbing processes are more or less the same in terms of flowsheet definition and operational principles.

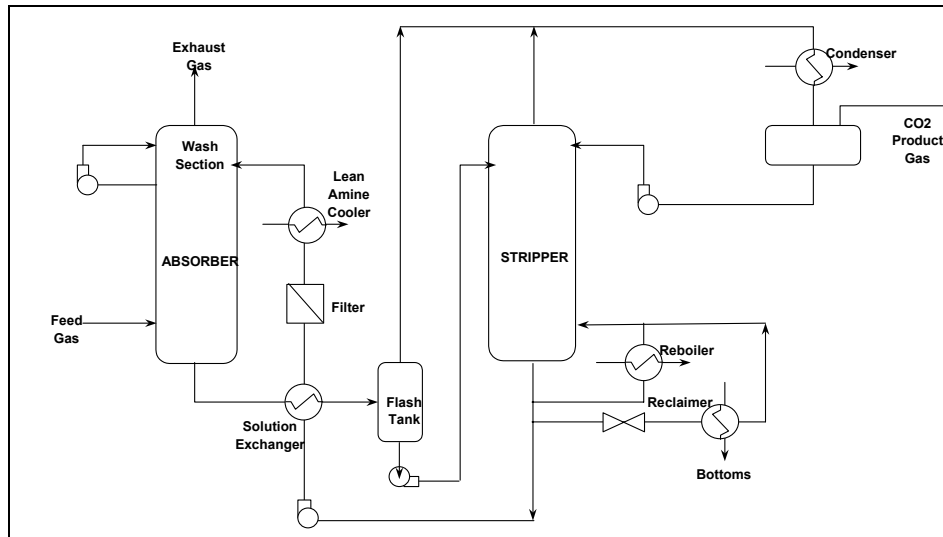


Fig. 8: Kerr-McGee/ABB Lummus Global MEA-based CO₂ recovery technology²

The recovery of carbon dioxide from the rich amine stream is a highly energy intensive process which requires substantial quantities of low pressure steam extraction from the power plant turbine cycle and high power usage for compressing large volumes of flue gases to overcome absorber pressure loss. A modified steam cycle for CO₂ separation by MEA absorption is shown in Figure 9.

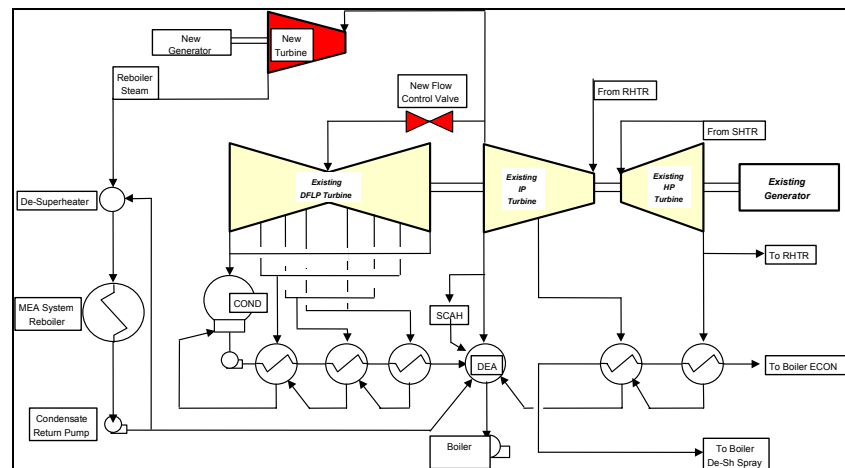


Fig. 9: Modified steam cycle for CO₂ separation by MEA absorption (Nsakala ya Nsakala *et al.*, 2001)

Amines are moderate bases, they will react with any acidic compounds to form amine salts. Usually these amine salts will be heat stable and will not dissociate in the amine stripping system. For this reason it is necessary, on economic grounds for all processes, to restrict flue gases SO₂ and NO₂ to low levels (typically 10 ppmv and 20 ppmw respectively). This creates additional processing requirements on the power plant gas treatment system. However the ALSTOM process “FLOWPAC” – based on wet limestone scrubbing technology – is available which can achieve 10 ppmv without any significant

² Courtesy of ABB Lummus Global

increase in costs compared to current installed technologies (Bill *et al*, 2004). Figure 10 shows the complete gas side process flow diagram for CO₂ separation by MEA absorption for a coal-fired boiler.

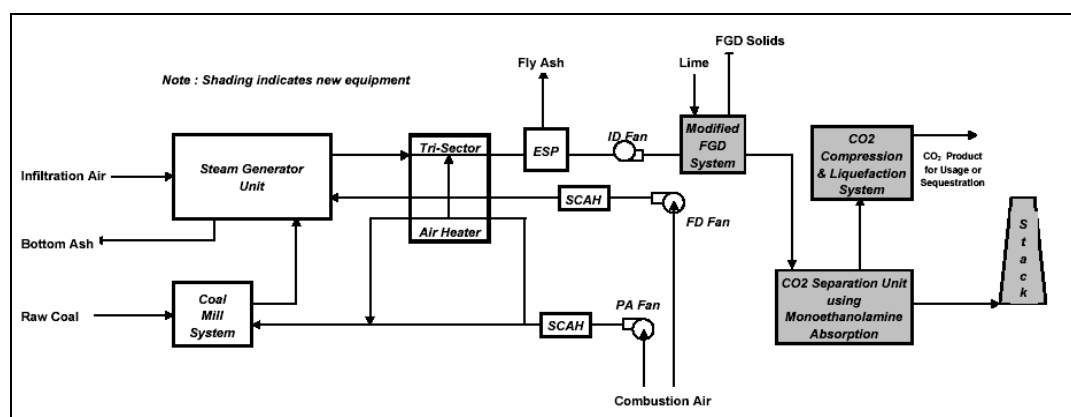


Fig. 10: Simplified gas side process flow diagram for CO₂ separation by MEA absorption (Nsakala ya Nsakala *et al.*, 2001)

5. Comparison between MEA and anti-sublimation processes

The two technologies being very different and each using a different kind of energy for the capture process: thermal for MEA and basically electrical for anti-sublimation, the comparison should be carried out with care in order to obtain comparable values (Clodic *et al.*, 2004).

Both capture systems should recover the CO₂ at 15 MPa with 90% CO₂ capture efficiency. The ambient conditions are 15°C, at sea level with 60% relative humidity.

Table 4 compares the power plant efficiency before and after capture as well as the energy penalties for two similar coal-fired power operating units each using a different CO₂ capture technology.

Table 4: Comparison between MEA and anti-sublimation processes (Clodic *et al.*, 2004b)

	MEA*	Anti-sublimation (L/H)**	
Power plant efficiency (%) (LHV)	36.66	33	
Power plant efficiency after capture (%) (LHV)	22.79	25.75	29.24
Energy penalty (points)	13.87	7.25	3.76
Energy penalty (%)	37.83	21.95	11.39

* The base case considered for the MEA capture unit is a 620 MWe boiler with an electrical power conversion efficiency of 36.66% and a flue gases composition of O₂-2.94 % v/v, N₂-68.45% v/v, H₂O-15.77% v/v, CO₂-12.83 % v/v and SO₂ < 10v ppm. The flue gases are considered at 58°C and 108.2 kPa.

** The base case considered for the anti-sublimation capture unit is a 660 MWe boiler with an electrical power conversion efficiency of 33% and a flue gases composition as specified in Table 2. The flue gases are considered at 60°C and 120 kPa. Two values are given in the columns to account for the high and low efficiency thresholds for CO₂ capture.

CO₂ capture by MEA penalizes the power plant efficiency by about 14 points so therefore reduces its output energy by 37.8%, while anti-sublimation, depending on the refrigeration system efficiency, reduces the efficiency by a value between 3.8 and 7.2 points and hence the output energy reduction is between 11.4 and 22%.

6. Conclusions

A new low temperature process for CO₂ capture has been designed and a mock up has been built. Calculations and experimental results show that this low temperature refrigerating system can compete with other CO₂ capture processes and is particularly well adapted for CO₂ capture on coal-fired boilers. The reduction in electricity conversion efficiency is limited and is comprised between 3.8 and 7.2%. Moreover, the global cooling process condensates and freezes the water vapor contained in the flue gases. This water condensation can be used for capturing other minor pollutants. One of the possible designs is to integrate the flue gases desulphurisation in the CO₂ capture process at low temperature. In this way, the cost of current flue gases desulphurisation could be avoided.

7. Acknowledgments

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