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# The 8th Trondheim Conference on CO2 Capture, Transport and Storage

# A Layout for the Carbon Capture with Aqueous Ammonia without Salt Precipitation

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# Abstract

Post-combustion carbon capture technologies seem to be necessary to realize the CO<sub>2</sub> mitigation policies internationally shared for the next future, despite none of them appears to be ready for full-scale applications. This work considers the aqueous ammoniabased process for a coal-fired Ultra Super Critical power plant. Two layouts are simulated with Aspen Plus employing the recently recalibrated Extended UNIQUAC thermodynamic model. The first one operates at chilling conditions, which yield to salt precipitation, and is taken as reference because already analyzed in previous studies. The second layout operates at cooled conditions, which does not yield any salt precipitation. The *Chilled* layout reveals low specific heat duty and *SPECCA* equal to 2.2 and 2.86 MJ/kgco<sub>2</sub>, respectively. In contrast, the *Cooled* layout presents a higher specific heat duty of almost 3 MJ/kgco<sub>2</sub> but, importantly, a lower *SPECCA* of 2.58 MJ/kgco<sub>2</sub>. The latter layout is a better choice also from the perspective of the plant operation since it does not present the salt precipitation.

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# 1. Introduction

The world energy production is expected to turn more and more sustainable in the future. Even in this scenario, the world energy demand will be mainly ensured by fossil fuels for decades. Fossils will have to be exploited effectively in terms of plant overall efficiency and environmental impact. In their turn, renewable sources will have to be

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Nomencl	ature		
Equipment abbreviations		ST	Stripper
AB	Absorber	WK	Water knockout
AC	Air-cooler	WT	Wash tower
CC	Contact cooling tower	Acronym	S
CM	Compressor	CAP	Chilled Ammonia Process
FGD	Flue gas desulfurization	FGD	Flue Gas Desulfurization
FN	Fan	USC	Ultra Super Critical
HC	Hydrocyclone	Symbols	
HX	Heat exchanger	$\eta_{\rm CO2}$	Carbon capture efficiency [-]
PM	Pump	η <sub>e</sub>	Net electrical efficiency [-]
PR	Purge	Ε	Specific CO <sub>2</sub> emission [kg <sub>CO2</sub> MWh <sub>e</sub> <sup>-1</sup> ]
RB	Reboiler	SPECCA	Specific Primary Energy Consumption
RC	Recuperator		for Carbon Avoided [MJth kgCO2 <sup>-1</sup> ]
RG	Regenerator	$q_{\rm CO2}$	Specific heat duty [MJ <sub>th</sub> kg <sub>CO2</sub> <sup>-1</sup> ]

implemented more diffusely in the energy infrastructure to allow independence from fossils in the far future. Coal will play most likely a primary role among the conventional sources, being the most abundant and diffuse of all. Several countries agreed on decreasing the carbon dioxide emission by anthropogenic activities. Hence, an effective technology for carbon capture and storage turns to be advisable because they are the only way to use fossil fuels with near to zero CO<sub>2</sub> emissions. In the short- to mid-term, post-combustion capture technologies are the most promising.

Post-combustion capture has the large benefit of being almost readily applicable to existing power plants, both coalor natural gas-fired. This carbon capture can be accomplished by adsorption or chemical absorption. Currently, the state of art is the post-combustion layout based on the chemical Monoethanolamine (MEA) as reported in the document of the EBTF (European Bench-marking Task Force) [1]. It is widely proposed also in non-conventional power plant as explained by Giuffrida et al. [2]. New families of amines are under investigation such as Piperazine [3] that gives promising results as reported by Kvamsdal et al. [4], even though it is not ready for the market. Alternatively to amines, the process named Chilled Ammonia Process (CAP), which is near to be commercialized by Alstom, is considered a feasible option. The company is testing and improving its viability targeting the carbon capture efficiency at 85% as reported by Lombardo et al. [5]. Previous works proposed by Valenti et al. [6, 7] show more attractive results for an ammonia-based capture plant with respect to a MEA-based one as confirmed by Jilvero et al. [8]. However, the chilled conditions of those studies include salt precipitation that can represent a complication in the management of the plant, despite solid formation may allow for a lower energy penalization as showed by Gazzani et al. [9] and studied by Gao et al. [10]. The issue of the ammonia slip is overcame adopting specific operating conditions as shown by Bak et al. [11], defining particular layouts as proposed by Valenti et al. [12] or adding metal ions as proposed by Li et al. [13].

The schemes of the CAP plant described by Alstom in 2007 [14] and studied by Valenti et al. [7] has been modified during the years. Kozak et al. [15] present an evolution of the first scheme of Alstom, three different schemes of plant are proposed in the parametric work [12]. The present investigation is based on the *Layout 2* studied in [12] and some changes on the plant are based on the recent information available in the work proposed by Lombardo et al. [5]. The thermodynamic model used for the electrolyte system is the Extended UNIQUAC proposed by Thomsen and Rasmussen [16]. It is implemented within the code Aspen Plus, and it is able to describe well the CO<sub>2</sub>-NH<sub>3</sub>-H<sub>2</sub>O system as showed by Darde et al. [17]. For the present work, a better calibrated Extended UNIQUAC is adopted.

The updated scheme of plant is recalculated based on the information of the parametric investigation conducted in previous work [12]. The resultant parameters are taken as the base case for the CAP. Here, a new parametric analysis is proposed. The aim is to determine the operating conditions of the updated ammonia-based capture plant that permit an effective performance without the drawback of salt precipitation. The performances of the capture plants are evaluated estimating how they affect the indexes of merit for a defined Ultra Super Critical (USC) power plant.

### 2. Reference case

The flue gas to be treated in the capture plant is obtained by a coal-fired power plant. The USC power plant adopted is the one described in [1]. Such document has the scope of establishing a consolidated common framework for international dissemination. The reference power plant has a net electric power output of 754 MWe and a net electric efficiency of 45.5%, both at nominal conditions. The carbon dioxide flow is about 160.7 kgco2/s at a concentration of 15.2 vol % on a dry basis. The reference capture plant is based on MEA. The performances are in Table 4.

#### 3. Thermodynamic model and process layouts

The USC power plant equipped with the CAP is divided into two major blocks: (i) the power and (ii) the capture block. The power block is treated as a whole, whereas the capture block is subdivided into islands: (i) exhaust chilling, (ii) absorption-regeneration-gas wash, (iii) carbon dioxide compression and (iv) ammonia removal.

The results for the carbon capture plant are obtained with the simulation software Aspen Plus implemented with the Extended UNIQUAC thermodynamic model. These simulations do not consider the last section called (iv) ammonia removal which it is supposed to reduce at trace the  $NH_3$  employing an acid water wash. The results of the integration of the capture plant with the reference EBTF case are simulated with a simplified model of the steam turbine.

#### 3.1. Validation of the better calibrated Extended UNIQUAC thermodynamic model

For the present work, the Extended UNIQUAC thermodynamic model is implemented in Aspen Plus. The model is calibrated with more experimental data and it is extended to higher temperature range, passing from 150°C to 200°C with respect to previous works. The validation of the implemented thermodynamic model for the system CO<sub>2</sub>-NH<sub>3</sub>–H<sub>2</sub>O in the region of interest against the experimental data available in open literature is conducted here. Just a limited number of results from a validation are visualized in Fig. 1, showing a very good agreement between computed and measured values, which is true for the other cases not illustrated.

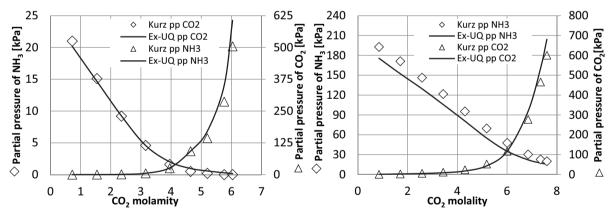


Fig. 1. Comparison of the results for the calculation via the Extended UNIQUAC thermodynamic model (indicated by Ex-UQ) of the partial pressure of  $CO_2$  and  $NH_3$ : on the left at 313 K in  $CO_2$ - $NH_3$ - $H_2O$  mixture 6.3 molal of  $NH_3$ , on the right at 353 K in  $CO_2$ - $NH_3$ - $H_2O$  mixture 11.8 molal of  $NH_3$ ; experimental data by Kurz et al. [18].

#### 3.2. Power Block

The effect of the steam extraction on the power generation is computed starting from a typical expansion curve of a low pressure turbine. The curve is assumed to be a straight segment connecting inlet and outlet of the turbine on an entropy-enthalpy diagram (Fig. 2). The extraction pressure along the curve is determined by the regeneration temperature allowing for a minimal temperature difference in the reboiler. Prior to entering the reboiler, the steam is

desuperheated with part of the liquid water exiting the reboiler itself. The extracted mass flow rate is defined by the energy balance over the reboiler for a given heat duty. The electric loss due to the steam extraction is computed as the power that would be generated by the extracted steam from the extraction state to the outlet state assuming that the expansion curve does not change. The integration of the exiting condensate with the power block, such as in the deaerator or in the pre-heating line, is not considered now. The condensate is instead directed to the condenser. The characteristic of the steam turbine are the same as the steam turbine of the EBTF cited before. The ratio of the electric power loss due to the stream extraction from the turbine and the heat duty as a function of the regeneration temperature is depicted in Fig. 2. At a temperature as low as 80°C a heat duty of 1 MWth corresponds to a power loss of 0.119 MWe. This loss grows rapidly to 0.166 at 100°C, 0.212 at 120°C and 0.256 MWe at 140°C.

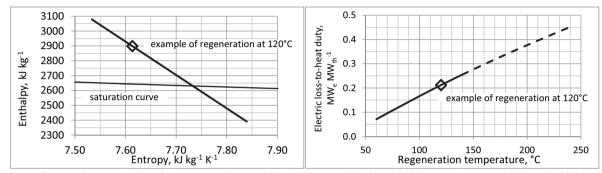


Fig. 2. Left: expansion curve in the enthalpy-entropy diagram of the low pressure turbine from which the steam is extracted. Right: ratio of electrical loss-to-heat duty as a function of regeneration temperature (above 140°C the curve is extrapolated because the computed pressure is higher than the inlet pressure). The diamond shows an example of a regeneration temperature at 120°C.

#### 3.3. Capture block

In this work the simulations with the equilibrium-based approach of the capture plant are carried considering not only the energy performances, but also the water and ammonia balance. Two layouts are proposed: a first one that operates with the absorption stage in chilled mode, as originally proposed by Alstom for CAP, and a second one that operates with the absorption stage in a cooled mode in which the temperature is higher than the first layout as proposed by Bonalumi et al. [19].

The *Chilled* layout, showed in Fig. 3, is equipped with a chilling plant that decrease the temperature of the all treated streams sent to the absorber at 7°C. The maximum temperature reached inside the absorber is around 18°C despite the exothermic reaction of absorption. This temperature promotes the salt precipitation in a wide range of concentrations of reactants. This configuration is an upgrade of the *Layout 2* proposed in [12]. The main differences are: (i) the condenser on the top of the regenerator to reduce the ammonia concentration of the CO<sub>2</sub> stream which

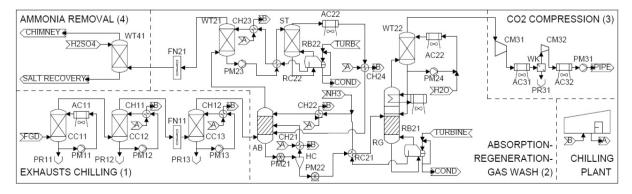


Fig. 3 Chilled layout: scheme of plant with stages for the decreasing of the absorption temperature obtained with a chilling plant

leaves the regenerator, (ii) the outlet stream exiting from the stripper (ST) that is sent in the absorber instead of in the regenerator (RG), this shrewdness allows the stripping of NH<sub>3</sub> at near ambient pressure.

The *Cooled* layout, shown in Fig. 4, is equipped with air-coolers to decrease the temperature to 20°C of the treated stream dispatched to the absorber. In this case the maximum temperature reached in the absorber is around 27°C. This temperature prevents the salts precipitation for a wide range of concentrations of the reactants. This layout is arranged modifying the *Chilled* one. The main differences are: (i) the substitution of the chillers with air-coolers (except for the CH 21) allows to reduce the electric consumption and to increase the temperature in the absorber, (ii) the hydrocyclone (HC) is not necessary, and (iii) a split fraction of the rich solution exiting the absorber is recycled to the ammonia water wash circuit (passing thru CH22) to minimize the purges and the make-up.

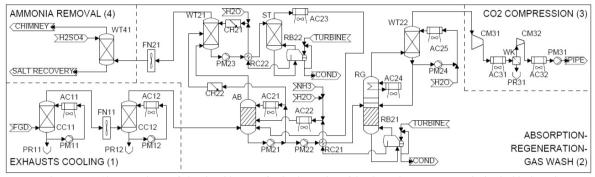


Fig. 4. Cooled layout: scheme of plant in with stages for the decreasing of the absorption temperature obtained with air coolers.

#### 3.4. Design parameters

The design parameters are: (i) ammonia initial concentration in the aqueous solution, (ii) ammonia-to-carbon dioxide ratio in the absorber, (iii) regeneration pressure, (iv) heat duty to the regenerator, (v) inlet tray of lean solution inside the absorber and (vi) recycling fraction of the rich solution to the top of the absorber. The ammonia-to-carbon ratio in the absorber is the ratio of the number of ammonia moles entering the reactor through the lean solution line and the number of carbon dioxide moles entering through the exhaust line. The recycling fraction is a mass percentage of the stream exiting from the bottom of absorber. The constraints on the plant are: (i) carbon capture efficiency set at 85%, (ii) the ammonia slip in the exiting gas from the water wash column (WT21) below 130 ppm, and (iii) the ammonia slip in the compressed carbon dioxide below 5 ppm. The chosen values are in Table 2. Carbon capture efficiency is defined as the ratio of the flow rates [kmol/s or kg/s] of the carbon dioxide exiting the compression island and of that entering the capture plant.

#### 3.5. Performance indexes

Commonly, the specific heat duty,  $q_{CO2}$  [MJ<sub>th</sub>/kg<sub>CO2</sub>] defined as the ratio of the reboilers heat duty [MW<sub>th</sub>] and the mass flow rate [kg/s] of effectively captured carbon dioxide, is utilized as performance index. However, such index does not include the information on the capture efficiency nor on the temperature at which the heat duty is required (or in equivalent terms the loss of electrical power from the steam turbine). Therefore, here another index is adopted, introduced by Campanari et al. [20], that solves the issues while sharing the same units. It allows so to compare plants characterized by different capture efficiencies, regeneration temperatures and electric efficiency penalties. The Specific Primary Energy Consumption for Carbon Avoided (*SPECCA*) [MJ<sub>th</sub>/kg<sub>CO2</sub>] is defined as:

$$SPECCA = \frac{H - H_{REF}}{E_{REF} - E} = \frac{3600^* (1/\eta - 1/\eta_{REF})}{E_{REF} - E}$$
(1)

where all parameters refer to either the power plant equipped with the carbon capture or the reference power plant without it: *H* is the heat rate  $[MJ_{th}/MWh_e]$ , *E* the specific CO<sub>2</sub> emission  $[kg_{CO2}/MWh_e]$ ,  $\eta$  [nondimensional] the net electrical efficiency and *REF* stays for reference. The reference values here adopted are included in Table 1. Moreover, as an indication, the *SPECCA* of a conventional MEA plant calculated by EBTF [1] exceeds 4 MJ/kg<sub>CO2</sub>. The last index is the net electric efficiency of the power plant with the post-combustion capture plant.

Parameter	Unit	Value	Parameter	Unit	Value
Air coolers			Heat exchangers		
Fluid end temperature	°C	20	Minimum temperature difference	°C	5
Relative pressure drop	%	0	Low pressure steam turbine		
Specific electric consumption	$MW_eMW_{th}^{-1}$	0.02	Inlet pressure	bar	4,5
<u>Ambient air</u>			Inlet temperature	°C	306
Temperature	°C	15	Outlet pressure	bar	0,05
Chilling plant			Outlet vapor title	%	93
Coefficient of performance	MWth MWe <sup>-1</sup>	5	Outlet velocity	m s <sup>-1</sup>	250
Specific electric consumption	$MW_eMW_{th}^{-1}$	0.20	Generator efficiency	%	98
Columns			Isentropic efficiency	%	88
Contact cooler pressure drop	bar	0,01	<u>Motors</u>		
Other column pressure drop	bar	0,03	Electro-mechanical efficiency	%	95
Compressors			Pumps		
Isentropic efficiency	%	85	Hydraulic efficiency	%	85
Last compressor end pressure	bar	80	Reboiler		
Fans			Steam superheated temperature	°C	5
Forced fan end pressure	bar	1,06	Steam subcooled temperature	°C	0
Induced fan end pressure	bar	1,06	Reference power plant		
Isentropic efficiency	%	90	Net electric power	MWe	754
Exhausts			Net electrical efficiency, $\eta_{el,REF}$	%	45,5
Mass flow rate	kg s <sup>-1</sup>	782	Specific CO <sub>2</sub> emission, E <sub>REF</sub>	kg <sub>CO2</sub> MWhe <sup>-1</sup>	763
Pressure	bar	1.04	Pipeline		
Temperature	°C	50	Delivery pressure	bar	110
Composition:	% (vol. wet)		Targets		
CO <sub>2</sub>		13,73	Max ammonia slip	ppmv	130
Inert (Ar, N <sub>2</sub> ,O <sub>2</sub> )		76,54	Treated gas	ppmv	10
H <sub>2</sub> O		9,73	Compressed carbon dioxide	ppmv	5

#### 4. Results and discussion

The results of the simulations of the capture plant layouts here investigated are integrated with the model of the power plant in order to assess the performance of the whole system.

# 4.1. Chilled layout results

The new scheme of plant and the newly-calibrated thermodynamic model allow to obtain a very low value for the specific heat duty and a very attractive value of *SPECCA*. The operating conditions are reported in Table 2. The CO<sub>2</sub> loading entering the absorber and the regenerator are respectively about 0.61 and 0.88 mol<sub>CO2</sub>/mol<sub>NH3</sub>. For this layout,

depicted in Fig. 5, the main electrical consumptions is the one related to the island *ABS-RGN-GW* (2) (about 64.4 MWe) because the presence of the chilling plan and the *Power block* island (47 MWe) as shown in Table 4.

#### 4.2. Parametric investigation for the Cooled layout

The influence of all six design parameters is well defined: some of the results obtained combining the parameters are shown in Fig. 5. The decrease of the regeneration pressure allows lower values of *SPECCA*. The decrease of  $NH_3$  concentration in the initial solution has remarkable benefits over the *SPECCA*. The ammonia-to-carbon dioxide ratio has an optimum value from the *SPECCA* perspective, as well the recycle fraction of the rich stream to the top part of the absorber. In particular, the inlet tray, above the middle one, plays a limited role, however the best tray individuated is the number 3 on an overall of 5 ideal trays, as shown at the lower part on the right of Fig. 5. The combination of the parameters that allow the minimum value of *SPECCA*, among the investigated, is in Table 2. The CO<sub>2</sub> loading entering the absorber and the regenerator are respectively 0.46 and 0.63 mol<sub>CO2</sub>/mol<sub>NH3</sub>.

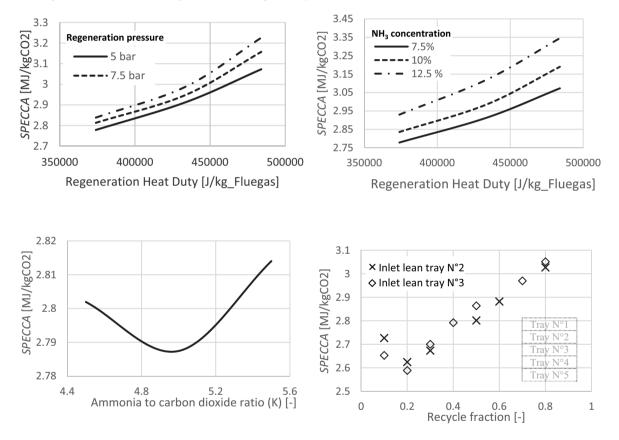


Fig. 5 Influence of the design parameters on the performance index.

#### 4.3. Detailed integration of the capture plant with the power plant

The electric consumption for the capture plants are reported in Table 3. The *Exhaust cooling* and the *ABS-RGN-GW* sections are more penalizing for the *Chilled* layout, due to the major consumption of the chillers. The *Power block* is more penalizing for the *Cooled* layout: a large contribution is due to the higher amount of NH<sub>3</sub> that must be recovered by the water wash section, while another contribution is due to the higher specific heat duty and the higher regeneration temperature that require more steam extraction at higher value of enthalpy from the turbine. Furthermore, the

*Compression* stage is more penalizing for the *Cooled* layout since the regeneration pressure is lower than in the *Chilled* layout. The results of the power consumptions of the capture plant integrated with the power plant are summarized in Table 4.

Table 2. Selected parameters for Chilled and Cooled layout obtained by means the parametric analysis.

Parameter	Unit	Chilled layout	Cooled layout
Ammonia initial concentration	%wt	20	7.5
Ammonia-to-carbon dioxide ratio	kmol kmol-1	3.2	5
Recycle	-	0.8	0.2
Tray	N°	5	3
Regeneration pressure	bar	20	5
Regeneration temperature	°C	95.4	105.6

Table 3. Electri	c consump	otion for the	Chilled layout and for the	<i>Cooled</i> lay	rout.
Electric power, $MW_{el}$	Chilled	Cooled	Electric power, MW <sub>el</sub>	Chilled	Cooled
Exhaust cooling (1)					
AC11	2,357	2,351	CH24	0,045	0,000
AC12	0,000	0,132	FN21	3,154	3,342
CH11	4,860	0,000	PM21	1,629	1.410
CH12	1,058	0,000	PM22	2,362	1,121
FN11	3,943	4,177	PM23	<0,001	0,003
PM11	0,597	0,592	PM24	0,010	0,010
PM12	0,201	0,142	Subtotal	<u>64,380</u>	<u>17,219</u>
PM13	0,102	0,000	Power block		
Subtotal	<u>13,148</u>	<u>7,394</u>	RB21	45,131	57,207
ABS-RGN-GW(2)			RB22	1,878	15,321
AC21	0,220	0,671	Subtotal	<u>47,009</u>	<u>72,528</u>
AC22	0,144	4.626	$CO_2$ Compression (3)		
AC23	0,018	1.770	AC31	0,226	0,326
AC24	0,000	0.952	AC32	0,775	0,957
AC25	0,000	0,018	CM31	6,771	15,421
CH21	36.349	2,801	CM32	6,019	14,825
CH22	20,310	0,495	PM31	1,784	0,652
CH23	0,139	0,000	Subtotal	<u>15,575</u>	<u>32.181</u>
			TOTAL LOSS	<u>140,112</u>	<u>129,323</u>

## 5. Conclusions

The work proposes an equilibrium-based study of the ammonia-based post-combustion carbon capture with the newly-calibrated Extended UNIQUAC implemented in Aspen Plus. Two schemes of plant, able to capture 85% of

CO<sub>2</sub>, are proposed. One operates at chilled condition and the design parameters are the ones previously presented by the authors. The other one operates at cooled conditions and a parametric analysis has permitted to determine a set of operative parameters at which corresponds a minimum value of *SPECCA* for this layout. The study indicates that:

- the ammonia-based technology confirms to be more attractive than the MEA-based technology;
- the ammonia-based technology require one of the lowest value of specific heat duty, 2.2 MJ/kgco2;
- the *Chilled* layout here proposed require a lower specific heat duty compared to the *Cooled* one, 2.2 MJ/kgco2 instead of almost 3 MJ/kgco2;
- the merit index *SPECCA* for the integrated capture plant with the power plant reveals that the *Cooled* layout is the more attractive configuration, in particular this one present a value of about 2.6 MJ/kgco2 with respect to the 2.9 MJ/kgco2 of the *Chilled* one;
- the *Cooled* layout combines the advantage of a moderate energy requirement with the absence of the solid formation.

Parameter	Unit	Reference	MEA	Chilled (with salts)	Cooled (without salts)	
Electric power loss	MWe	NA	198.9	140.1	129.3	
Net electrical power	MWe	754.0	562.4	613.9	624.7	
Net electrical efficiency, $\eta_{el}$	%	45.5	33.5	37.05	37.70	
Heat Duty specific	MJ/kgCO <sub>2</sub>	NA	3.70	2.19	2.98	
Specific CO2 emission, E	kg <sub>CO2</sub> MWhe <sup>-1</sup>	763	104	141.4	138.9	
SPECCA	MJ/kgCO <sub>2</sub>	NA	4.16	2.86	2.58	

#### Table 4. Performances of the compared capture plants

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