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## Amine-impregnated Alumina Solid Sorbents for CO<sub>2</sub> capture. Lessons learned

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### Abstract

The application of Amine-impregnated Alumina Solid Sorbent Carbon Capture is a suitable option to increase CO<sub>2</sub> capture efficiency and to reduce by several percentage points the efficiency penalty of CCS in power plants. These sorbents require less regeneration energy due to the reduction in water content and the higher heat capacity of solids. The objective is to demonstrate that the use of amine-impregnated alumina solid sorbents is a suitable option to increase CO<sub>2</sub> capture efficiency and to reduce several percentage points the efficiency penalty caused by the capture system in the power plant. The proposed innovative sorbent consists in amines supported on high surface area and high porosity solid materials, such as alumina and silica-alumina. Good results have been achieved. Important high porosity support makes possible to obtain high CO<sub>2</sub> capture capacities over 50 mg CO<sub>2</sub>/g of sorbent. As a consequence, the combination of this CCS option with a coal power plant may reduce the efficiency penalty down to 7 efficiency points. This figure could make feasible the impregnated amine solid sorbent as a future and promising option for CO<sub>2</sub> capture.

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**Keywords:** Solid Sorbent; CO<sub>2</sub> capture; energy penalty; Thermal integration

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## 1. Introduction

Fossil fuel power plants provide 56% of the total electricity demand and, among them, coal power plants have a contribution of 29% in electricity generation. Energy forecasts show that fossil fuels will remain the main primary source for electricity generation in the medium and long term, retaining a share in power generation of at least 40-50% in 2030. For this reason the 'Energy roadmap 2050' report highlights that carbon capture and storage (CCS), if commercialized, will have to contribute significantly to European power generation with contributions around 19–24% in usual scenarios.

According the Strategic Research Agenda of the European Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP), some of the key research issues to solve for postcombustion CCS are [1]:

- Insufficient experience for power plant application on large-scale and special requirements due to flue-gas conditions.
- High energy demand/penalty for regeneration of the solvent and energy requirements for CO<sub>2</sub> compression.
- Full process integration and optimization for power generation.
- Adsorption system with high-throughput under oxygen environment.

Among different CCS technologies, several post-combustion methods have been proposed to separate CO<sub>2</sub> from the flue gas stream in large point-sources, such as coal-fired power plants and energy intensive industries. Amine chemical adsorption is the most developed since there is great experience in the chemical and oil industries for the removal of CO<sub>2</sub> from gas streams. However, this process has a significant energy penalty due to the high energy requirements in the regeneration step.

The accomplishment of lower energy penalties in the CO<sub>2</sub> capture process is crucial to the goal of implementing CCS at industrial scale. Gas-solid adsorption is considered to be one of the most promising technologies. A variety of physisorbents, such as zeolites and activated carbons, may be used to remove CO<sub>2</sub> from flue gases, although the CO<sub>2</sub> adsorption with these sorbents is strongly influenced by temperature, pressure and presence of moisture and contaminants such as SO<sub>x</sub> and NO<sub>x</sub>. Modifications in the surface of the porous materials by incorporating different functional groups are considered very promising techniques to improve some characteristics of solid sorbents. These chemisorbents present great potential to reduce the energy penalty and to increase the capture capacity and CO<sub>2</sub> selectivity compared to amine processes, being alkali carbonates and amine functional groups the most common ones.

The success of chemisorbents is therefore dependant on the development of new materials with high adsorption capacity, high CO<sub>2</sub> selectivity, durability and relatively fast kinetics of sorption and desorption. In this context, the demonstration of the behaviour of the sorbents under real flue gas conditions is an important step. A hypothetical solid sorbent with a working capacity of 4.3 mmol/g and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 150 could reduce the capital cost for the adsorption system and CO<sub>2</sub> compression, leading to capture costs around \$30/tonCO<sub>2</sub>.

Amine-impregnated Alumina Solid Sorbents for CO<sub>2</sub> capture (ASC2) project has focused on several of the most important recommendations ZEP report for the deployment of CCS in the European Union (EU). It would contribute to increase the experience of pilot plant operation with commercial power plant flue gases and to reduce the energy demand for regeneration (improving the efficiency of power plants with CCS), through full process integration, power plant optimization and high sorbent efficiency for CO<sub>2</sub> capture including improved degradation behavior under different flue gas conditions (effect of other pollutants and oxygen content). CCS process integration into the power plant and its optimization are presented in this paper.

### Nomenclature

CC	Capture cycle
CCS	Carbon Capture and Storage
CT	Compression train
FGD	Flue Gas Desulphurization
MEA	Monoethanolamine

## 2. Amine-impregnated Alumina Solid Sorbents for CO<sub>2</sub> capture

Solid amine sorbents were first used for CO<sub>2</sub> capture in closed environments [2, 3]. These materials have important advantages: reduction of sorbent/amine requirements due to a high surface contact area and the elimination of the water that reduces the regeneration energy and improves the process efficiency when compared with MEA scrubbing [4-6]. Different amines and supports have been studied for CO<sub>2</sub> capture, such as silica [7, 8], different polymer types [9, 10], zeolites [11, 12], carbon fly ashes [13] or porous carbons [14]. In this case, the material selected as a support is porous alumina due to its high resistance to steam and good mechanical and thermal stability [9, 15-18].

The configuration of the reactor system is also crucial to the process and several configurations have been studied, such as fixed-beds [6] or fluidized-beds [7, 8, 19]. One possibility to scale-up the concept would be using two interconnected fluidized beds reactors for exchanging the solid sorbent between sorption and regeneration reactors. In ASC2 process, the flue gas is introduced in the sorption reactor where the amine impregnated sorbent selectively adsorbs the CO<sub>2</sub>. For continuous processes, the CO<sub>2</sub> sorbent must be regenerated to be used repeatedly. This step takes place at the regeneration reactor. While sorption reactor (SR) was defined as a circulating fluidized bed; the slow regeneration times made unfeasible to adopt the same hypothesis for the regeneration one (RR); so a fixed bed with complete sorbent regeneration has been assumed in this case.

## 3. Methodology. Process Integration.

Process integration between the power plant and the capture process is required to avoid an important energy penalty in the regeneration step. The objective of this integration is to provide the energy required for sorbent regeneration while implying the lowest possible penalty to the power plant production. A 500 MWe supercritical power plant has been defined and modelled with ASPEN PLUS®. It includes four low-pressure and four high-pressure heaters with deaerator. The main characteristics of the power island are shown in Table 1, it remains without variations in order to analyse the impact of the CO<sub>2</sub> capture cycle in the power production. The coal used is detailed in Table 2.

As the CO<sub>2</sub> capture cycle is a low-temperature process, the area of interest for the analysis is the low pressure zone of the power plant. The turbine bleeds that provide initially the energy to low pressure part are the heat sources to consider in the analysis. The capture plant has been dimensioned after the flue gas leaving the power plant. It is assumed that the flue gas has been through FGD processes and enters the system without SO<sub>x</sub>. The flue gas entering the CO<sub>2</sub> capture process is detailed in Table 3. As the presence of steam in the flue gases may enhance the nitrosamines formation there is a flue gas condensation before entering the capture cycle. This condensation should be cost-effective, which implies the feasibility to perform the process by means of water cooling; so a limit condensation temperature of 25°C has been set. With the flue gas conditions, this objective temperature implies that the amount of condensed water can be a 51% of the amount of water in flue gas, which makes the water content in the gas entering the sorption reactor as low as 3%. After the condensation, the flue gas needs to increase their temperature and pressure before entering the sorption reactor. The temperature increase has been taken into account in the integration process and a fan has been added just before the sorption reactor to increase the pressure of the gas to the reactor conditions.

Table 1. Supercritical power plant characteristics.

	600.3	°C
Live steam	250	bar
	350	kg/s
	610	°C
Reheat steam	49.58	bar
Deaerator pressure	12.3	bar
Condenser pressure	0.045	bar
Q <sub>coal</sub>	960.07	MW <sub>th</sub>
Net power	481.13	MWe
Efficiency	46.91	%
Flue gas	422.2	kg/s

Table 2. Coal composition.

% C	72.04
% H	4.68
% N	1.67
% O	7.36
% S	0.65
% H <sub>2</sub> O	8.1
% Ash	14.2
LHV [kJ/kg]	25,372

Table 3. Power plant flue gas composition before and after condensation.

	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>	O <sub>2</sub>	Total flue gas	T	P
	[kg/s]	[kg/s]	[kg/s]	[kg/s]	[kg/s]	[°C]	[bar]
Before condensation	91.82	15.73	299.5	15.14	422.2	180	1.027
After condensation	91.82	7.60	299.5	15.14	414.1	25	1.027

A scheme of the capture system is shown in Figure 1. The capture plant has been modelled as two reactors, a sorption one and a regeneration one. The sorption reactor (circulating fluidized bed) operates at 42.5°C and 1.3 bar. The value of sorption capacity is 54 mg CO<sub>2</sub>/g sorbent, however as residence times in circulating fluidized beds are lower than in fixed beds, a 78% of sorption capacity has been assumed [20]. A global capture efficiency of 80% was considered.

The energy streams of the capture plant are listed in Table 4. These streams are divided between heat sources (type hot) and heat sinks (type cold). As can be seen, the more demanding energy stream is the heat that must be provided to the regeneration reactor (RR), which works at 82.5°C and 0.13 bar

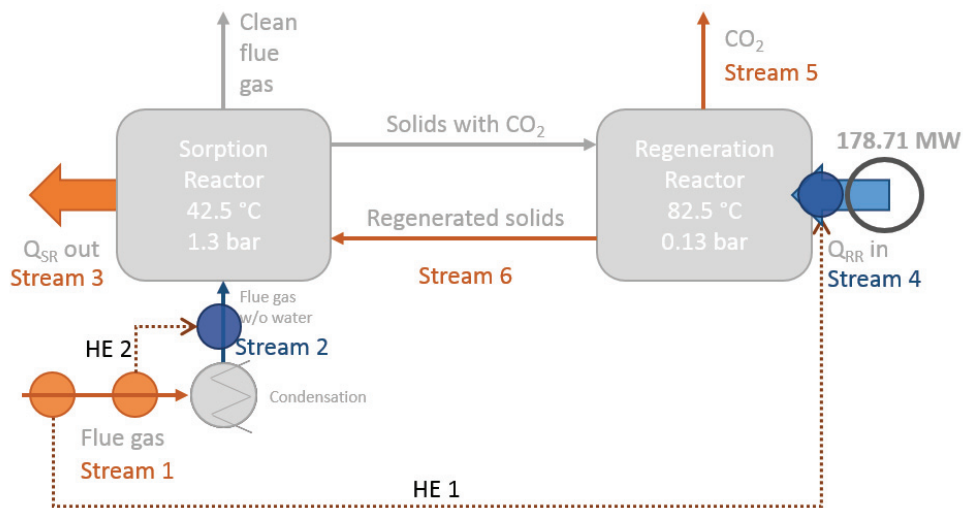
Fig. 1. Diagram scheme of CO<sub>2</sub> capture principle

Table 4. Energy streams of the capture system and power plant

	Stream	T <sub>in</sub> [°C]	T <sub>out</sub> [°C]	Q [MW <sub>th</sub> ]	Type
1	Flue gas before condensation	180.00	37.70	100.65	HOT
2	Flue gas after condensation	25.00	39.41	6.26	COLD
3	Sorption heat	42.60	42.50	126.00	HOT
4	Regeneration heat	82.50	82.60	240.60	COLD
5	Captured CO <sub>2</sub>	82.50	50.00	2.11	HOT
6	Solids from RR to SR	82.50	52.00	112.03	HOT

Captured CO<sub>2</sub> requires to be conditioned prior to the transport phase. Thus, a five-stage compression train (CT) with intercooling has been studied to take also into account their energy requirements. The intercoolers of the compression train may provide an amount of energy in a temperature range adequate for the integration with the power plant and the CO<sub>2</sub> capture cycle. The power requirement of the compression train to proceed with the 73.45 kg/s of CO<sub>2</sub> amounts 45.13 MWe.

When defining the integration between the different systems, two main objectives were observed [21]: to provide the energy required for sorbent regeneration while maintaining the flow and final temperature of the condensate stream. Two different configurations have been analysed. A first one comprising only the power plant and the CO<sub>2</sub> capture plant, and a second one including also the compression train as part of the process. In this work, internal energy integration is proposed. Steam bleeding is not used to supply the energy demand in the capture cycle. Only the energy from flue gas is used for preheating before sorption reactor and to provide regeneration heat, figure 2. The integration methodology calculates, according to pinch analysis, the amount of heat that can be internally exchanged, as well as the hot and cold energy requirements that must be externally provided. Then, by applying a systematic procedure [22], a heat exchanger network is defined. It evaluates the amount of energy to satisfy the hot energy requirements of the heat sinks and calculates the heat exchanger network and the new parameters of the plant.

The regeneration reactor requires an important amount of heat. According to the temperature of the regeneration reactor (82.5 °C) the penalty to provide energy to the capture plant has been calculated for the base case. The power produced by the system when deriving steam for sorbent regeneration amounts 435.95 MWe; which implies a baseline energy penalty of 45.19 MWe, see Table 5. Once this value is established, the objective of the integration between the power plant and the capture plant is to reduce this energy penalty as much as possible. For the configuration comprising power plant, capture cycle and compression train, the baseline penalty is doubled, due to the 45.13 MWe required by the compression train.

The high energy requirements of the regeneration reactor (Q<sub>RR</sub>=240.6 MW<sub>th</sub>) is supplied by steam turbine bleeds. There are two IP (intermediate pressure) available bleeds, an assessment has been performed to define the best option. According to this analysis the optimum option to supply the 240.60 MW<sub>th</sub> required for sorbent regeneration has to be provided by lower IP bleed alone (103.8 kg/s). If high IP was used, in spite a lower steam mass flow, an additional reduction in steam power of 21.5 MWe was obtained in calculations. An important amount of steam has to be derived to the capture cycle. This amount may lead to changes in the last turbine steps to adapt them to the new requirements of the cycle.

Table 5. Energy integration results. Base case and CO<sub>2</sub> capture without integration

Power plant + capture cycle (CC)		Power plant + capture cycle (CC) + Compression train (CT)				
W <sub>net</sub> base case [MWe]	Q <sub>RR</sub> [MW <sub>th</sub> ]	W <sub>net</sub> base case. No integration [MWe]	Energy penalty [MWe]	CT energy penalty [MWe]	W <sub>net</sub> base case. No integration [MWe]	Energy penalty [MWe]
481.13	240.60	435.95	45.19	45.13	390.82	90.31

With these results, net efficiency of the power plant reduces to 38.1% that is a penalty of 8.8 efficiency points. It is not a relevant figure so it can be concluded that low temperature solid sorbent technology for CO<sub>2</sub> capture is a promising option for efficient and low-cost CCS.

For the internal integration, figure 2 shows as flue gas (Stream 1) is used to provide part of the energy required by the regeneration reactor, thus lowering the amount of steam required from the turbines. The remaining energy of Stream 1 can be used to increase the temperature of Stream 2 to adapt flue gases temperature in the absorption inlet. The remaining regeneration heat will be provided by intermediate pressure steam bleed. This internal integration allows reducing the energy penalty of the system as depicted in Table 6. Power plant is able to produce 11.6 MWe additional power (45.19-33.56), 447.56 MWe, and in consequence the net efficiency of the power plant increases up to 39.24%, figure 4. With this number, the efficiency penalty has been reduced to 7.7. There are room for improvements and with additional research the impact of low temperature solid sorbent technology could be reduced in a near future allowing a rapid and economic deployment of this CCS technology.

Table 6. Energy integration results. Base case and CO<sub>2</sub> capture with integration

W <sub>net</sub> base case [MWe]	Q <sub>RR</sub> [MWth]	W <sub>net</sub> base case with CC internal integration [MWe]	Energy penalty [MWe]
481.13	178.71	447.56	33.56

When including the compression train, figure 5, the amount of heat exchanged and their distribution regarding Stream 1 is the same than before. Due to the inclusion of the new heat sources, there is a certain amount of additional heat that lowers the requirements of the regeneration reactor (from 178.1 MWth to 152.88MWth). Nevertheless, the compression train also implies an additional energy penalty due to their energy consumption, as shown in Table 7, which must be taken into account.

Table 7. Energy integration results. Base case and CO<sub>2</sub> capture with integration including CO<sub>2</sub> compression

W <sub>net</sub> base case [MWe]	Q <sub>RR</sub> [MWth]	W <sub>net</sub> CC internal integration [MWe]	Energy penalty [MWe]	CT energy penalty [MWe]	W <sub>net</sub> CC+CT internal integration [MWe]	Total energy penalty [MWe]
481.13	152.88	452.42	28.72	45.13	407.29	73.84

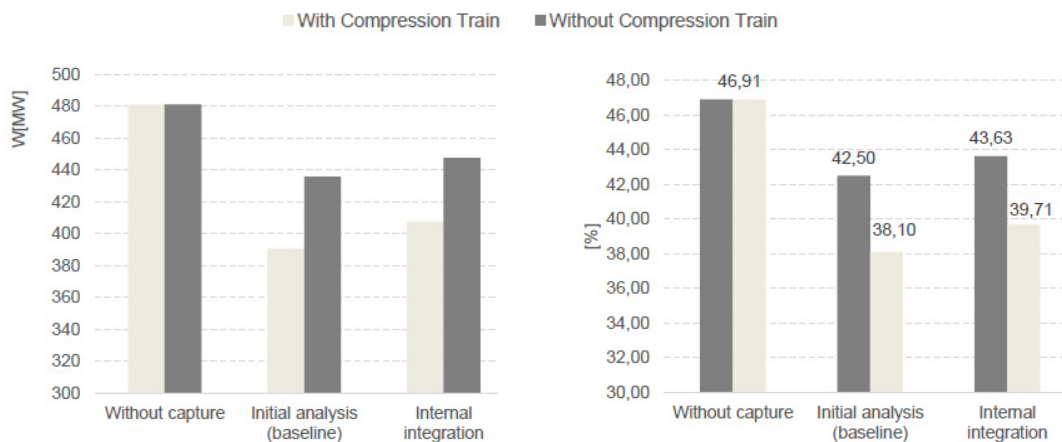


Fig. 4. Comparison of power plant power output and net efficiency

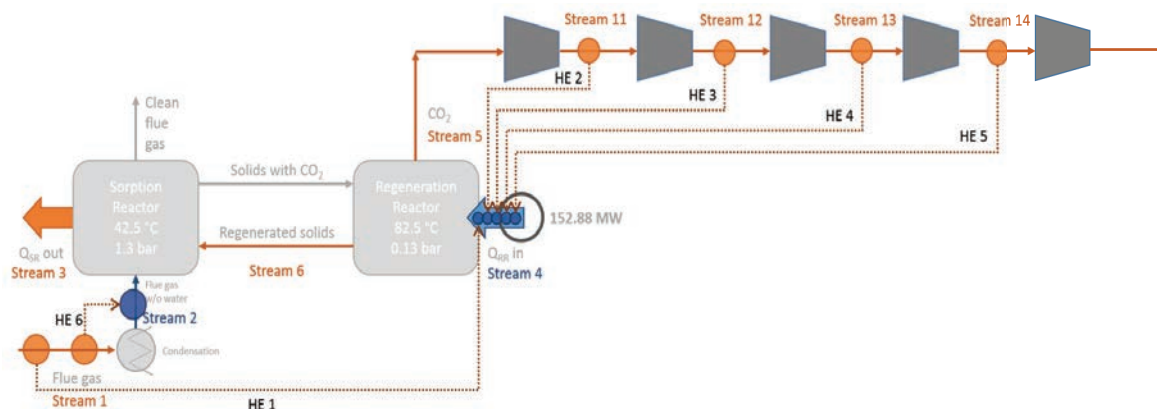


Fig. 5. Proposed internal energy integration with compression energy streams

#### 4. Conclusions

Amine-impregnated Alumina Solid Sorbent Carbon Capture is a future and promising option for CO<sub>2</sub> capture as it is able to reduce by several percentage points the efficiency penalty of CCS in power plants. If high porosity supports could be developed and CO<sub>2</sub> capture capacities over 50 mg CO<sub>2</sub>/g of sorbent are possible, the energy integration results show that, in a first approach, the efficiency penalty could be reduced down to 7.7 efficiency points but with additional work this figure may be reduced down to 6 efficiency points.

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