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INTRODUCTION

This document analyses the energy release in the carbonation reaction as well as how this energy is used within the process. Several carbonator side configurations are assessed with the aim of obtain preliminary conclusions and to define the framework for the process design stage. The carbonator side analysis includes the reactor and the auxiliary equipment (heat exchangers, coolers, etc.) for the proper operation of the plant.

This deliverable summarizes the work under execution in *Task 4.1 "Carbonator-power cycle integration"*. This task is divided in the following activities or subtasks:

- ST 4.1.1. Carbonator side configuration as a function of the power cycle (industrial scale)
- ST 4.1.2. Carbonator side configuration for the SOCRATCES prototype
- ST 4.1.3 Support to tasks 4.2, 4.3, 4.4. Iterative interaction

Results from subtasks ST4.1.1 and ST4.1.2 are included in this deliverable aiming to support the iterative process expected in ST 4.1.3. **The document serves as reference for others task in SOCRATCES, namely, task 4.2, task 4.4, task 2.3 and task 5.1.**

The deliverable is structured in two well-differentiated sections. The first one is dedicated to the analysis of the carbonation energy release for a design at industrial scale, and it covers the main process configurations to produce energy from the stored products. The second part of the document is focused on the carbonator side analysis at the scale of the SOCRATCES prototype demonstrator.

The document here presented has been developed within the SOCRATCES project under the confidentiality rules of the project and consortium.

1. CARBONATOR SIDE CONFIGURATION AS FUNCTION OF THE POWER CYCLE (INDUSTRIAL SCALE)

Process integration plays a key role on the adaptation of the CaL technology to the solar power plant. Despite that the CaL technology was already conceptualized for solar energy storage in the late 1970s [1] and solar calcination has been tested since the 80s [2], [3], process integration schemes have not been proposed until a few years ago.

Figure 1 shows a conceptual CSP-CaL process integration scheme for the carbonation side. When power generation is needed, stored CaO and CO_2 (calcination products) are brought together to the carbonator, where energy is released through the carbonation reaction. Previously, both streams are preheated through a heat exchanger network to take advantage of the high-temperature streams exiting the carbonator and to avoid thermal stresses and cooling on parts of the reactor with the inhibition and reversion of the reaction. The higher temperature of streams entering the carbonator, the lower heat consumed in the reactor to bring the reactants to the carbonator temperature, and therefore a higher amount of energy can be used for power production by means of a power cycle integrated with carbonator.

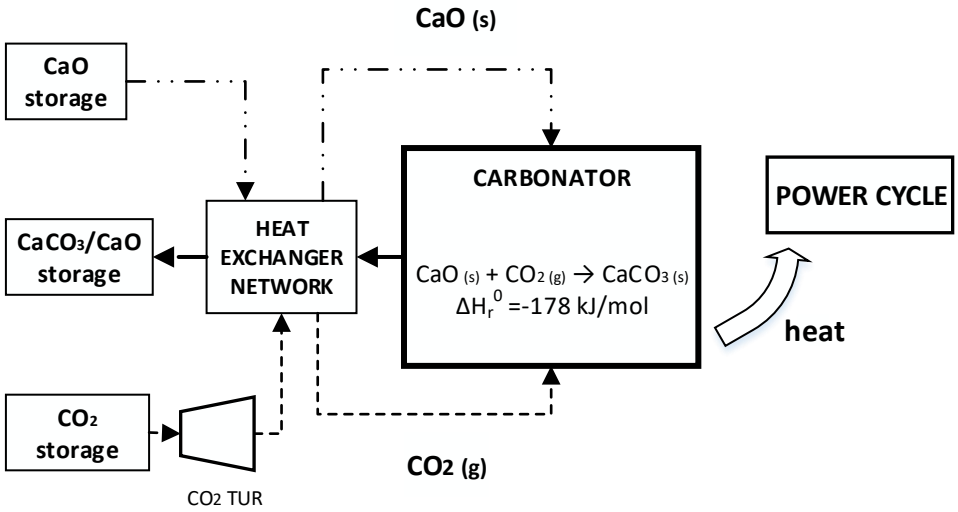

Figure 1. Conceptual CSP-CaL process integration scheme for the carbonation side

Several carbonator side schemes have been already proposed in the literature. In [4] was studied a CSP-CaL integration scheme in which the heat produced in the carbonator reactor is used for power generation through a CO_2/air open cycle**.** An alternative to the open Brayton cycle, a regenerative CO_2 closed Brayton cycle was proposed by Chacartegui et al. [5]. Alternatives schemes for regenerative CO_2 closed Brayton cycle considering direct integration and low-temperature solids storage were proposed by [6]. In [7] were explored several power cycles integration schemes within the CSP-CaL plant. A recent work [8] analyzed configuration schemes by considering high-temperature solids storage, for daily storage, and carbonator-power cycle direct integration by means of CO_2 closed Brayton cycle. A recent study has been published for the integration of a CSP-Calcium looping for uninterrupted power production, and through energy storage [9]. Solar calcination through a volumetric gas receiver, and a closed CO_2 Brayton cycle is considered for thermochemical energy storage and power production during both the day and the night. In this study, a preliminary design, integration and simulation of such a

process plant is performed via a direct heat integration and low to high temperature solids storage, leading to a maximum global plant efficiency of 31.5 %.

From these works, this section goes further in the process scheme definition. Novel schemes considering both low and high temperature solids storage are compared. Moreover, the indirect integration of power cycles is analyzed from a carbonator energy release point of view, which is the base for task 4.2. In this deliverable, four integrations schemes are proposed and analyzed for industrial scale plants (**Table 1**):

Table 1: proposed carbonator side schemes for industrial scale plant

Id.	Model describe in	Description
HT-D	Section 1.1.2	**High-temperature** solids storage **Direct** integration: CO_2 closed Brayton cycle
HT-I	Section 1.1.3	**High-temperature** solids storage **Indirect** integration: carbonation heat to external power cycle
LT-D	Section 2.1.1	**Low-temperature** solids storage **Direct** integration: CO_2 closed Brayton cycle
LT-I	Section 2.1.2	**Low-temperature** solids storage **Indirect** integration: carbonation heat to external power cycle

Since the performance of potential schemes are analyzed, this document provides useful information about the advantages, challenges, constraints and opportunities of the CSP-CaL integration under a wide range of operation conditions. Moreover, novel and previously-proposed modified schemes are simulated by considering the same assumptions and parameters, which leads to an accurate comparison between them.

For simulating the carbonator schemes at industrial scale, unless otherwise specified, CaO conversion (X) in the carbonator is assumed to be X=0.15 at stationary conditions, which is a value previously used in literature [8]. Once developed a more detailed carbonator model, which is the core of task 2.2 to be finished in next months, the new model will be integrated within the process schemes to achieve a more detailed calculation.

Main assumptions considered in the modelling process for all schemes proposed are summarized in Table 2.

Unless otherwise indicated, carbonator-power efficiency (η_{power}) is calculated as follow:

$$\eta_{\mathrm{power}} = \frac{\text{Net electric power produced } [\mathrm{MW_e}]}{\text{carbonation thermal power released } [\mathrm{MW_t}]}$$

Table 2. Main assumptions considered in the carbonator side integration

Group	Parameter	Component	Value
Turbomachinery	Isentropic efficiency	Main CO_2 turbine (M-TURB)	0.9
		Main CO_2 compressor (M-COMP)	0.87
		High pressure storage turbine (HPS-TURB)	0.8
	Mechanical-electric efficiencies	Main CO_2 turbine (M-TURB)	0.98
		Main CO_2 compressor (M-COMP)	0.98
		CO_2 turbine (HPS-TURB)	0.96
	number of intercooling/reheating stages	Main CO_2 compressor (M-COMP)	2
		CO_2 turbine (HPS-TURB)	2
	Intercooling/reheating temperature	High pressure storage compressor (M-COMP)	40ºC
		High pressure storage turbine (HPS-TURB)	65/100 ºC
Heat exchangers	minimum temperature difference	gas-gas HX	15 ºC
		CO_2-cooler	15 ºC
	Pressure drops	coolers	1%
		Gas-gas (both sides)	5%
		solid-gas HX (both sides)	3%
Reactors	Heat losses	Carbonator	1% of heat transferred
	Temperature	Carbonator	850 ºC
	Pressure	Carbonator (Direct integration schemes)	3.5 bar
	Pressure	Carbonator (Indirect integration schemes)	1 bar
Storage vessels	CO2 storage conditions	CO_2 vessel	75 bar 25 ºC
Heat rejection	Parasitic power consumption	All coolers	0.8% of heat released
Solids transport	Energy consumption		20 MJ/ton

1.1. Process schemes: high-temperature energy storage (HT)

The temperature in the storage vessels constrains the configuration of the process scheme and the efficiency of the processes.

The low-temperature storage allows the increase of the storage period, even seasonal energy storage. Due to the high temperatures in both calciner and carbonator reactors, a low temperature storage involves a large streams temperature drop along the entire cycle (**Figure 2**). It requires an optimized heat integration to achieve an adequate system efficiency.

Moreover, if high volumes of CO_2 tanks are not possible, the CO_2 must be stored under high pressures (P>75 bar) and reduced temperatures, to stored it as liquid. It implies to the CO_2 temperature of the CO_2 stream before storage, coming from calciner as much as possible to reduce the power consumption in the compressor.

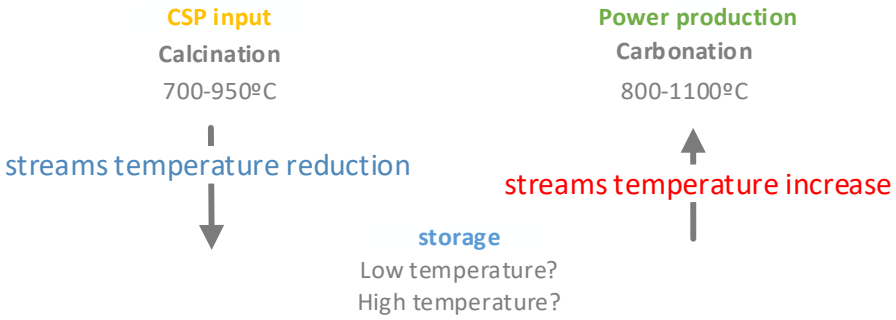

Figure 2: CO2 temperature changes along the CSP-CaL cycle

Another possibility, which is investigated throughout this section, is **storage the solids at high temperature**. In this case the process scheme is simplified by requiring fewer heat exchangers due to a lower temperature difference between the reactors and the storage. On the other hand, seasonal storage cannot be considered because of the temperature losses. However, the CSP-CaL could be operated under a solar multiple SM, defined as the ratio of the solar thermal power to the power block design thermal input, similar than in current CSP plants (SM~2-3) [10], and taking into account the higher energy storage density of CaL system in comparison with molten salts [8], a high-temperature CaL storage system of similar size could allow to store energy along longer periods, even days, than the current 16 hours in state of art molten salts - based CSP plants [11].

1.1.1 Direct integration scheme for high temperature energy storage (HT-D)

This scheme shows a potential carbonator side configuration at industrial scale considering high temperature (HT) energy storage and direct (D) integration of the power block through a CO_2 closed Brayton cycle. A similar scheme was previously proposed by [8]. To enable direct integration of the power block, the CO_2 mass flow rate entering the carbonator is above stoichiometric need for CaO carbonation. Storage is considered at high pressure (75 bar) to reduce the size of CO_2 vessel. Once energy production is demanded, CO_2 from the vessel is send to a secondary CO_2 turbine for expanding the gas from storage to the carbonator pressure. In comparison with [8], the scheme showed in **Figure 3** introduces a new gas-gas heat exchanger (HE7) to preheat the CO_2 exiting the storage vessel as previous step to the expansion up to the carbonator pressure. Heat is provided by CO_2 stream coming from the turbine. This allows a reduction in the cooling and heating requirements. The CO_2 stream entering the carbonator is

preheated through two serial heat exchangers which takes advantage of the high-temperature streams exiting the carbonator. Thus, HE6 is a gas-gas heat exchanger that works as regenerator in the CO_2 Brayton cycle and HE5 is a gas-solid heat exchanger. CaO stream coming from the storage tank at high temperature directly enters the carbonator. Main equipment is described in Table 3.

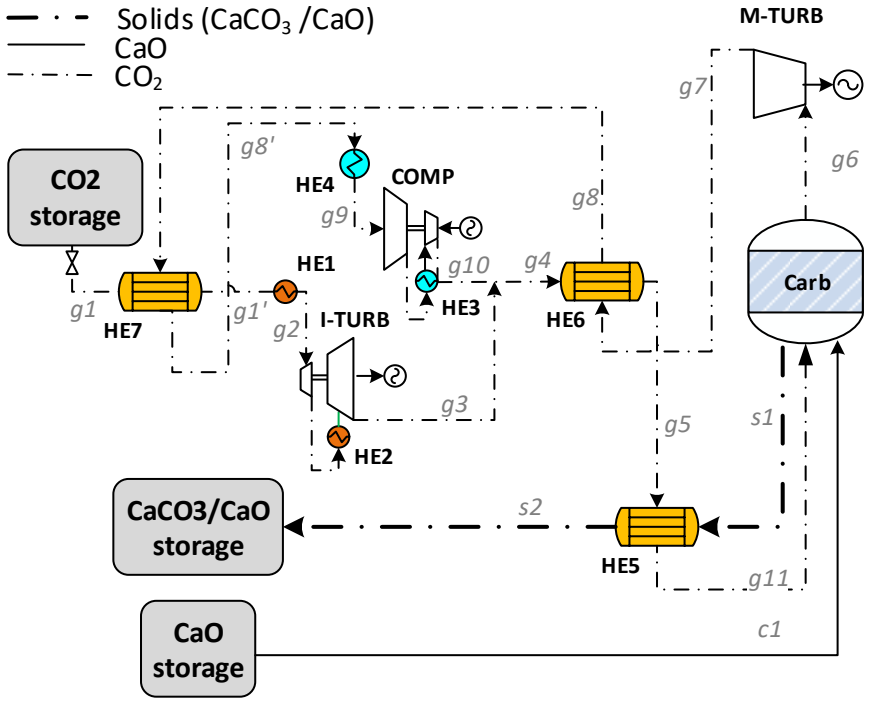

Figure 3: High-temperature solids storage. Direct integration. (HT-D) scheme

The process scheme has been configured avoiding solid-solid heat exchangers, which are not developed at industrial scale. As can be seen in ***Figure 3***, two heaters (HE1 and HE2) and two coolers (HE3 and HE4) would be needed in the process, which involves the associated consumption of utilities. The electric consumption for heat rejection and supply is assumed as 0.8% of heat released [12]. At this regard, it is important take into account that the power cycle modelling is not considered in this work (this issue will be studied in WP4, task 4.2) which means that cooling and heating needs could be reduced by integrating streams from the power cycle (i.e. turbine extractions for heating).

Table 3. HT-D scheme (Figure 3) equipment description

Equipment	Type	Description
COMP	Intercooled low-pressure compressor	The outcome CO2 stream of the main turbine at atmospheric pressure must be compressed until carbonation pressure to close the Brayton cycle. Two stages intercooled compression stages with equal pressure ratio are considered.
HE1	Heater	This heater is required to increase the inlet turbine temperature from storage temperature to 130^{0}C of set point.
HE2	Heater	This heater is required by the inter-heated turbine (I-TURB) to provide the require heat to increase the inlet temperate of the CO2 stream at each stage of the turbine

HE3	Cooler	Cooler required by the inter-cooled compressor (COMP) to reduce the temperature of the CO2 stream entering each stage.
HE4	Cooler	Heat integration among streams is insufficient to satisfy cooling requirement of the Brayton cycle so this cooler is needed to reduce the temperature at compressor inlet.
HE5	Solid-gas heat exchanger	This equipment enables heat integration between process streams. The solids stream *s1* leaves the carbonator at high temperature and a part of its enthalpy is recovered in this equipment to heat up the gas stream *g5* to enter the carbonator at highest possible temperature.
HE6	Gas-gas heat exchanger	Regenerator of the Brayton cycle. This equipment increases the temperature of the CO2 stream before recovering heat from solids existing the carbonator.
HE7	Gas-gas heat exchanger	This heat exchanger integrates both, highest pressure and lowest pressure streams aiming to reduce cooling and heating requirement before entering COMP and I-TURB.
I-TURB	Intermediate CO_2 turbine	Inter-heated turbine to reduce the pressure of the CO2 stream from CO2 tank (*supercritical conditions: 75bar and ambient pressure*) to carbonation pressure. 2 stages interheated compression stages with equal pressure ratio are considered.
M-TURB	Main CO_2 turbine	CO2 turbine of the Brayton cycle for direct integration of the power block.

The scheme represented in **Figure 3** has been simulated in ASPEN PLUS™ commercial software to analyse main stream and heat balance results, which are included in Table 4:

Table 4. Carbonator side HT-D integration scheme. Main results

Stream results							
Stream	P [bar]	T [ºC]	m [kg/s]	Stream	P [bar]	T [ºC]	m [kg/s]
g1	75,00	25	5,65	g8	0.95	92.11	90.90
g1’	74,97	77,11	5,65	g8’	0.92	77.61	90.90
g2	74,22	130	5,65	g9	0.90	40	90.90
g3	3.73	41.10	5.65	g10	3.7332	79.3327	90.90
g4	3.70	77.11	96.55	g11	3.4125	725.8616	96.55
g5	3.55	630.65	96.55	c1	1	700	48
g6	3.50	850	90.90	s1	1.2	850	53.65
g7	1	674.34	90.90	s2	1.17	645.7369	53.65

Heat exchangers thermal power		
ID	Heating [MW]	Cooling [MW]
HE-1 (Heater)	0.39	-
HE-2 (TURB)	0.54	-

HE-3 (COMP)	-	-6.49
HE-4 (Cooler)	-	-3.09
HE-5 (HEN)	11.18	-11.18
HE-6 (HEN)	57.64	-57.64
HE-7 (HEN)	1.21	-1.21
Electric power		
ID	Consumption [MW]	Generation [MW]
COMP	9.74	-
I-TURB	-	-0.74
M-TURB	-	-19.42
Auxiliaries solids transport	0.48	-
Auxiliaries cooling	0.005	-
Performance results		
Energy to preheat the carbonation reactants [MW]		7.77
Energy released in the carbonator to the power cycle [MW]		14.32
carbonation thermal power released [MW_{carb}]		22.09
$\eta_{\text{power}} = \frac{\text{Net electric power produced}}{\text{carbonation thermal power released}}$		0.45
Extra cooling demand [MW/MW_{carb}]		0.59
Extra heating demand [MW/MW_{carb}]		0.042

As can be seen in **Table 4**, a 45% of the energy released by the exothermic carbonation is converted to electric power. The process scheme is highly dependent on the solids temperature coming from the storage tank, since the lower storage temperature the higher amount of carbonation heat that must be used to preheat the reactants (**Figure 4**). By considering CaO conversion X=0.15, if solids are provided to the carbonator at temperatures below 385ºC, all the heat is required to preheat the solids carbonation, and heat release in carbonator is not enough to produce electric power. In the case of X=0.07 the minimum temperature is around 625ºC.

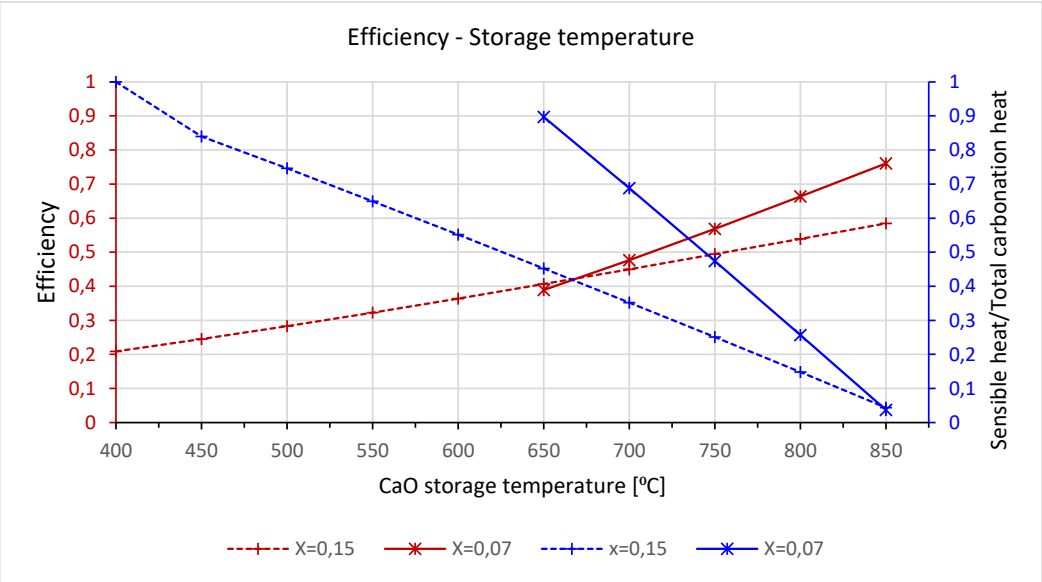

Figure 4: Influence of solids storage temperature (HT-D scheme)

Main consideration of the High-Temperature Direct (HT-D) scheme

- *This scheme takes advantage of the high-temperature of the stored CaO, which allows to introduce the solids in the carbonator directly, avoiding a complex gas-solid heat exchanger network.*
- *Thermal integration of process streams allows a reduced extra cooling and heating requirements in the system. Cooling requirements are 0.59* MW *per* MW *of power released in the carbonation* (MW_{carb})*, which can be provided by water or air at ambient temperature (minimum cooling set point of* 40 ºC*). A small extra heating requirement of 0.042* MW/ MW_{carb} *must be supplied at maximum temperature of 125* ºC*, which would allow use waste heat from the power cycle.*
- *In spite that CaO and CO_2 enter the carbonator at high-temperature, a high amount of heat released in the carbonation is used to preheat the reactants. Thus, by considering CaO storage at* ***385ºC****, all the released energy in the carbonation is used to preheat reactants and therefore this temperature stablishes a limit in the storage temperature to use this scheme.*
- *If the conversion of CaO is reduced to X=0.07; to release the same amount of carbonation heat (22,09* MW*), 93.5* kg/s *of CaO should enter the reactor (instead 48 kg/s as in the base case) and therefore the sensible heat to be transferred to the entering reactants increases. Thus, the minimum solids storage temperature considered for this scheme is 625* ºC*. At this temperature almost, all heat released in the carbonator is transferred as sensible heat to reactants.*

- *Solids (a mixture of $CaCO_3$ and CaO) exiting the carbonator side to the storage tank are at high-temperature, which simplifies the heat integration in the calciner side. The higher temperature of solids entering the calciner the higher amount of solar energy that can be stored, since the heat requires to bring the solid up to the calciner temperature is reduced.*
- *The direct integration based on a high-temperature Brayton regenerative cycle allows a high-power production from the heat released in the carbonation, a 45% the heat released in the exothermic reaction is converted to electric power. Taking into account that solids are stored from the calciner side at a maximum of 950 ºC), the higher temperature of solids entering the carbonator the higher amount of electric power production.*

1.1.2 Indirect integration scheme for high temperature energy storage (HT-I)

In this new scheme the carbonator side configuration at industrial scale considers high-temperature (**HT**) energy storage and indirect (**I**) integration of the power block through a heat exchanger that can be coupled with an externally heated power block (Rankine cycle, supercritical CO2, Stirling…). Accordingly, the scheme is divided in two well differentiated parts: the carbonator side scheme and the power cycle scheme which are mutually dependent through the heat exchange process and related output variables. **Figure 5** shows a schematic of the proposed HT-I configuration.

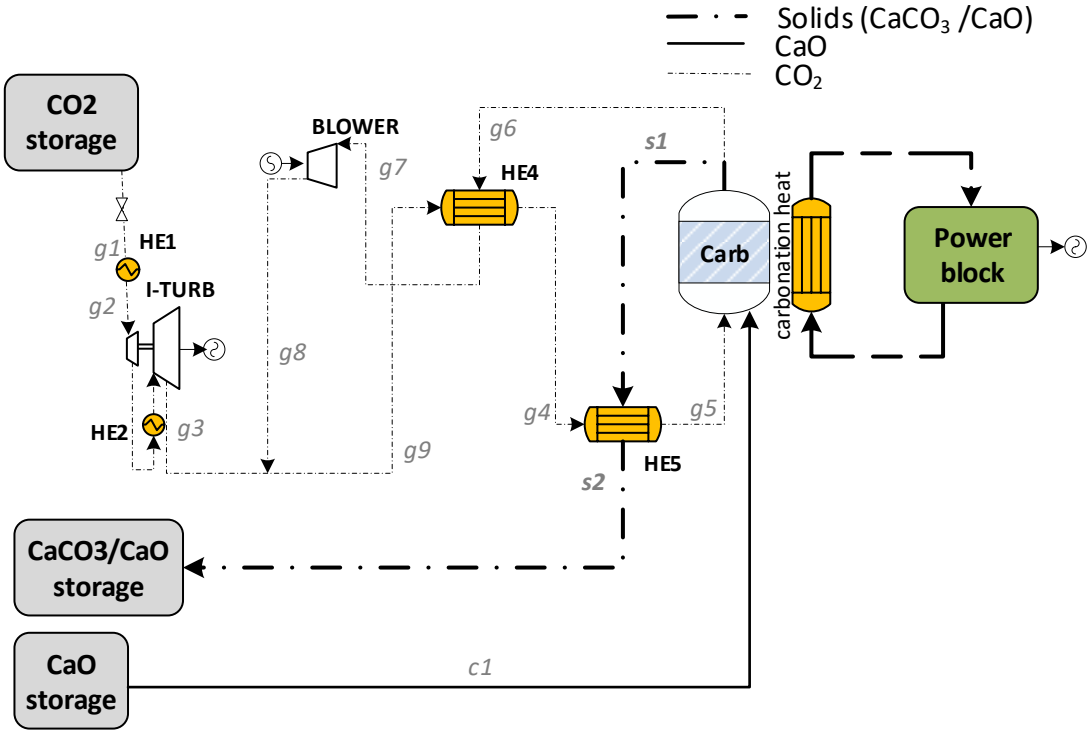

Figure 5. High-temperature solids storage. Indirect integration. (HT-I) scheme

Power cycle indirect integration can be carried out with a higher CO_2 flow in the carbonator than the stoichiometric value. The CO_2 in excess is used as heat carrier fluid which exchange the carbonator energy taken in a gas-gas heat exchanger located downstream of the reactor. This was previously analyzed by [7]. However, in the present work a different strategy is proposed. As represented in **Figure 5**, the heat exchanger to the power cycle is configured as a jacket in the reactor. In this case, the CO_2 entering the carbonator is the stochiometric value increased by 10% to ensure a proper fluidization of the solids in the reactor. Thus, in comparison with the HT-D scheme, the amount of CO_2 being recirculated is much lower. This scheme considers isothermal operation of the reactor. In this sense, since carbonation is an exothermic reaction which delivers thermal power, this power should be extracted in order to keep existing streams from carbonator under isothermal conditions (850 ^{o}C). In this scheme the exothermic energy delivered from carbonation is transferred to the heat exchanger to heat up the working fluid of the power block.

In the indirect integration carbonation can be carried out under atmospheric conditions, since a certain CO_2 pressure ratio is not needed for the power block operation.

The description of required equipment identified in **Figure 5**, is included in **Table 5**. Note that HE4 heat exchanger could not be interesting from an economic perspective due to the reduced

stream flow of CO_2 exiting the carbonator, and the related small amount of thermal power for heating.

Table 5. Initial scheme (Figure 4) equipment description

Equipment	Type	Description
BLOWER	Electrical	The blower is required to overcome the pressure drop of the CO2 circulating throughout the heat exchangers network. *In this scheme the carbonation unit operates at ambient pressure, thus the compressor included in the direct integration scheme has been replaced by a blower.*
HE1	Heater	This heater is required to increase the inlet turbine temperature from ambient value to 130ºC of set point.
HE2	Heater	This heater is required by the inter-heated turbine (I-TURB) to provide the require heat to increase the inlet temperate of the CO2 stream at each stage of the turbine
HE4	Gas-gas heat exchanger	HE4 integrates both, hot and cold CO2 streams by cooling down the hot stream (much lower than the hot one) previously to entering the blower, preheating the cold CO2 stream before entering HE5
HE5	Solid-gas heat exchanger	This heat exchanger enables to heat up the cold CO2 stream existing preheater H4 until carbonation temperature
I-TURB	Intermediate CO_2 turbine	Inter-heated turbine to reduce the pressure of the CO2 stream from CO2 tank (*supercritical conditions: 75bar and ambient pressure*) to carbonation pressure.

Main simulation results are included in **Table 6.**

Table 6. Carbonator side HT-I integration scheme. Main results

Stream results							
Stream	P [bar]	T [ºC]	m [kg/s]	Stream	P [bar]	T [ºoC]	m [kg/s]
g1	75	25	5,6506	G7	0,95	38,5815	0,5651
g2	74,25	130	5,6506	G8	1,1373	40	0,5651
g3	1,1373	21,9204	5,6506	C1	1	700	48
g4	1,0804	114,8049	6,2157	S1	1,2	850	53,6506
g5	1,048	835	6,2157	S2	0,97	758,559	53,6506
g6	1	850	0,5651				

Heat exchangers thermal power		
ID	Heating [MW]	Cooling [MW]
HE-1 (Heater)	1.59	-
HE-2 (TURB)	0.75	-
HE-3 (COMP)	-	-0.006
HE-4 (HEN)	0.51	-0.51

HE-5 (HEN)	5.05	-5.05
Electric power		
ID	Consumption [MW]	Generation [MW]
COMP	0,007	-
I-TURB	-	-1,01
Auxiliaries solids transport	0.48	-
Auxiliaries cooling	0	-
Performance results		
Energy to preheat the carbonation reactants [MW]	7.17	
Energy released in the carbonator to the power cycle [MW]	14.92	
carbonation thermal power released [MW_{carb}]	22.09	
Estimated power production (45% efficiency power block)	6.71	
$\eta_{power} = \frac{\text{Net electric power produced}}{\text{carbonation thermal power released}}$	0.33	
Extra Cooling demand [MW/MW_{carb}]	0	
Extra Heating demand [MW/MW_{carb}]	0.11	

The influence of CaO storage temperature is analysed in **Figure 6**. Results are similar than in the previous configuration (HT-D). By considering CaO conversion of X=0.15, solids storage temperature must be well above of 400ºC to produce a significant amount of electrical power.

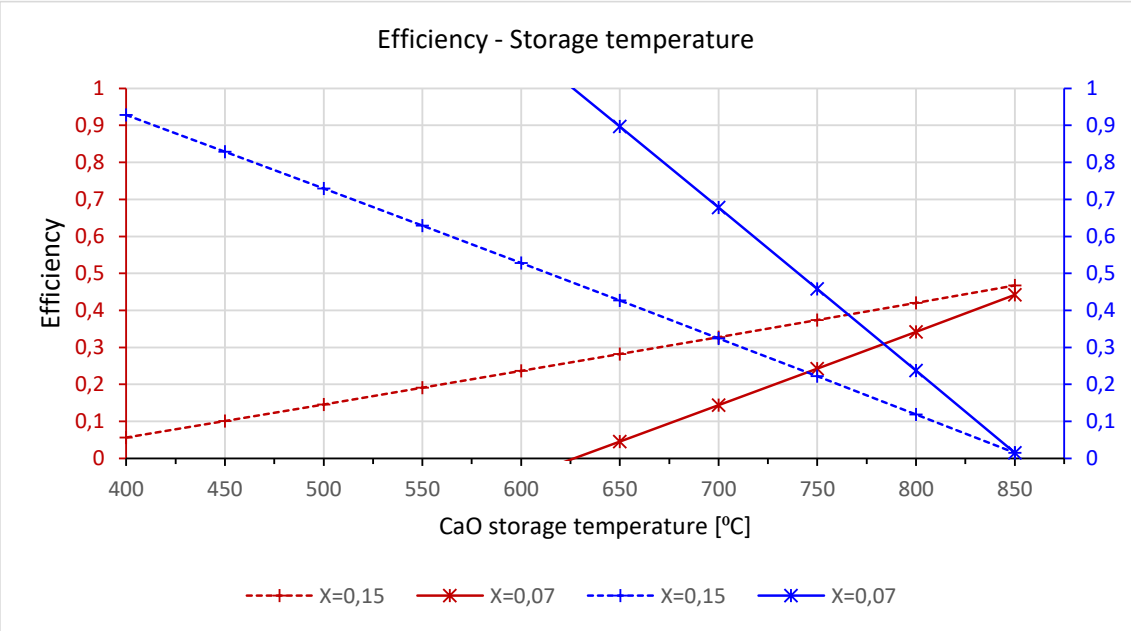

Figure 6: Influence of solids storage temperature (HT-I scheme)

The amount of CO_2 being recirculated by the closed loop is assessed in **Figure 7.** As may be seen, the higher amount of CO_2 recirculating the lower efficiency.

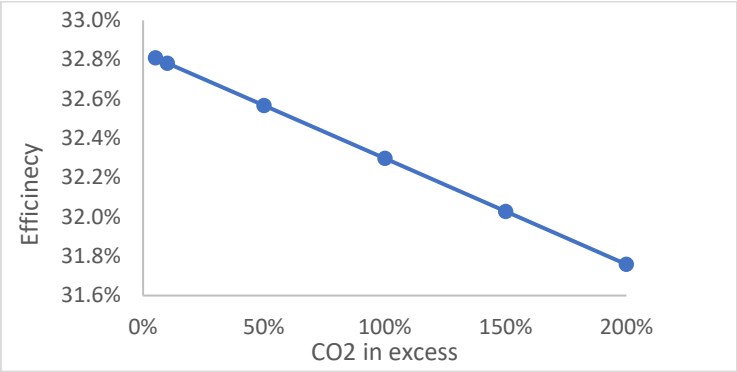

Figure 7: Influence of CO_2 in excess (HT-I scheme)

Main consideration of the High-Temperature Direct (HT-I) scheme

- *This integration scheme coupled to the high temperature of CaO storage tank makes possible to reduce cooling and heating requirements in the system.*
- *The net heating thermal power after the integration of streams is 0.11* MW/MW *carb. There is no need of cooling power.*
- *There is also a minimum storage temperature to enable electric power production under this configuration. This value increases when the conversion factor decreases since the sensible heat to be transferred to reactants is higher. Thus, minimum CaO storage temperatures of 337.1 and 626.4 are necessary by considering X=0.15 and X=0.07 respectively.*
- *The indirect integration allows a high-power production from the heat released in the carbonation, a 33% of the heat released in the exothermic reaction is converted to electric power. The higher temperature of solids entering the carbonator the higher amount of electric power production. Results are obtained for w the thermal efficiency of the power block of 45%.*
- *This scheme allows operation at ambient pressure in the carbonator, which makes easier the operation of the reactor.*
- Some components, at the HE4 heat exchanger could not be of interest from an economic perspective due to the reduced flow of CO_2 exiting the carbonator, and the associated amount of thermal power recoverable for heating.

1.2. Process schemes: low temperature energy storage

The possibility of long term energy storage is one of the most interesting features of thermochemical systems. Storing solids at ambient temperature avoid thermal losses allowing a more efficient decoupling of solar energy to power production, which would lead to a full capacity factor of the plant and to use high solar resource availability in some periods in others with a reduced one. In contrast, a more complex heat exchanger network would be necessary to increase as high as possible the reactants temperature at carbonator inlet to avoid thermal stresses and operation problems in carbonator.

1.2.1. Direct integration scheme for low temperature energy storage (LT-D)

An optimized process scheme based on low temperature (**LT**) solids storage direct integration (**D**) of the carbonator-power cycle was proposed by [5]. The scheme, showed in **Figure 8**, is used in the present document for comparison with other direct-indirect integration schemes.

In this scheme, the CO_2 stream from storage vessel is mixed with the CO_2 stream coming from the power loop previously to pass through a heat exchangers train (HE6, HE7 and HE8) which optimizes heat recovery at low temperature. The CO_2 exiting the turbine is divided in two streams passing through two heat exchangers (HE6 and HE8) in parallel while the hot solids exiting the carbonator pass through heat exchangers HE5 and HE7, reaching the solids storage tank at low temperature (~100ºC). This also involves the need for an optimized heat exchanger network in the calciner side to increase the solids temperature at calciner inlet. **Table 7** describes the main equipment in the LT-D scheme. Main simulation results are included in **Table 8.**

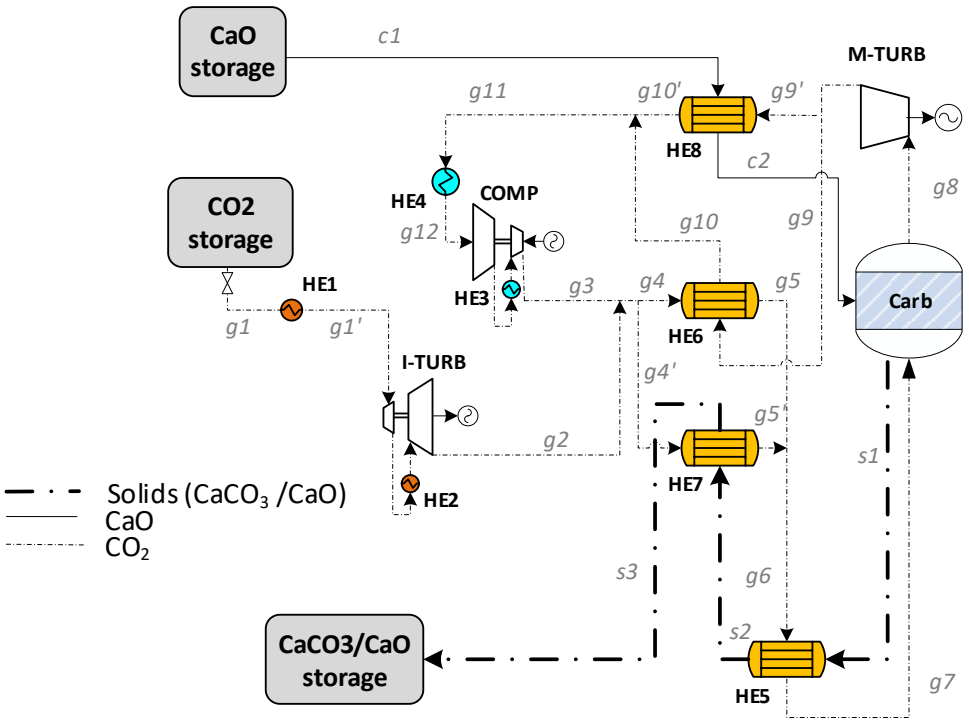

Figure 8. Low-temperature solids storage. Direct integration (HT-I). Adapted from [5].

Table 7: LT-D scheme (Figure 8) equipment description

Equipment	Type	Description
COMP	Intercooled low-pressure compressor	The CO_2 outlet stream of the main turbine at atmospheric pressure must be compressed until carbonation pressure to close the Brayton cycle. Two stages intercooled compression stages with equal pressure ratio are considered.
HE1	Heater	This heater is required to increase the inlet turbine temperature from storage temperature to 130^{o}C of set point.
HE2	Heater	This heater is required by the inter-heated turbine (I-TURB) to provide the require heat to increase the inlet temperate of the CO2 stream at each stage of the turbine
HE3	Cooler	Cooler required by the inter-cooled compressor (COMP) to reduce the temperature of the CO2 stream entering each stage.
HE4	Cooler	Heat integration among streams is insufficient to satisfy cooling requirement of the Brayton cycle so this cooler is needed to reduce the temperature at compressor inlet.
HE5	Solid-gas heat exchanger	This equipment enables heat integration between process streams. The solids stream *s1* leaves the carbonator at high temperature and a part of its enthalpy is recovered in this equipment to heat up the gas stream *g6* to enter the carbonator at highest possible temperature.
HE6	Gas-gas heat exchanger	This equipment increases the temperature of the CO2 stream from the gas stream exiting the carbonator.
HE7	Solid-gas heat exchanger	This heat exchanger takes advantage of the hot solids to preheat the CO_2 entering the carbonator.
HE8	Solid-gas heat exchanger	The solids flowing to the carbonator at low temperature are preheated with the CO_2 stream exiting the turbine. This is a close solid-gas heat exchanger, in order to avoid partial carbonation of the solids before entering the reactor.
I-TURB	Intermediate CO_2 turbine	Inter-heated turbine to reduce the pressure of the CO2 stream from CO2 tank (*supercritical conditions: 75bar and ambient pressure*) to carbonation pressure. Two stages interheated compression stages with equal pressure ratio are considered.
M-TURB	Main CO_2 turbine	CO2 turbine of the Brayton cycle for direct integration of the power block.

Table 8. Carbonator side LT-D integration scheme. Main results

Stream results							
Stream	P [bar]	T [^{oo}C]	m [kg/s]	Stream	P [bar]	T [^{o} C]	m [kg/s]
g1	75	25	5,65	g9	1	673.4	50.09
g1’	74,25	130	5,65	g9’	1	673.4	40.25
g2	3.80	17	5,65	g10	1	108.5	50.09
g3	3.80	82.12	90.34	g10’	1	50.39	40.25
g4	3.80	78.46	49.40	g11	1	83.30	90.34
g4'	3.80	78.46	46.59	g12	1	40	90.34
g5	3.61	658.4	49.40	c1	1	25	48
g5'	3.68	658.4	49.40	c2	1	658.4	48
g6	3.61	658.4	95.99	s1	1	850	53.65
g7	3.55	741.5	95.99	s2	1	673.4	53.65
g8	3.5	850	90.34	s3	1	101.5	53.65

Heat exchangers thermal power		
ID	Heating [MW]	Cooling [MW]
HE-1 (Heater)	1.59	-
HE-2 (TURB)	0.55	-
HE-3 (COMP)	-	-5.71
HE-4 (Cooler)	-	-3.45
HE-5 (HEN)	9.77	-9.77
HE-6 (HEN)	30.93	-30.93
HE-7 (HEN)	29.16	-29.16
HE-8(HEN)	27.03	-27.03

Electric power		
ID	Consumption [MW]	Generation [MW]
COMP	9.68	-
I-TURB	-	-0.74
M-TURB	-	-19.22
Auxiliaries solids transport	0.48	-
Auxiliaries cooling	0.073	-

Performance results	
Energy to preheat the carbonation reactants [MW]	9.60
Energy released in the carbonator to the power cycle [MW]	12.49
carbonation thermal power released [MW_{carb}]	22.09

$\eta_{power} = \frac{\text{Net electric power produced}}{\text{carbonation thermal power released}}$	0.44
Extra cooling demand [MW/MW_{carb}]	0.41
Extra heating demand [MW/MW_{carb}]	0.10

Since solids enter the carbonator side at low temperature, the LT-D configuration is highly dependent of solids amount to be send to the carbonator, which is influenced by the CaO conversion. Thus, for a certain thermal production by carbonation, the lower the CaO conversion, the higher number of solids that must be introduced in the reactor. This implies that, if the CaO conversion is lower than a certain minimum value, the energy released in the carbonator is not enough to preheat the stored solids from low temperature to the carbonation temperature, and therefore it would not be possible to produce electric power. **Figure 9** shows the effect of the CaO conversion on the carbonator side efficiency.

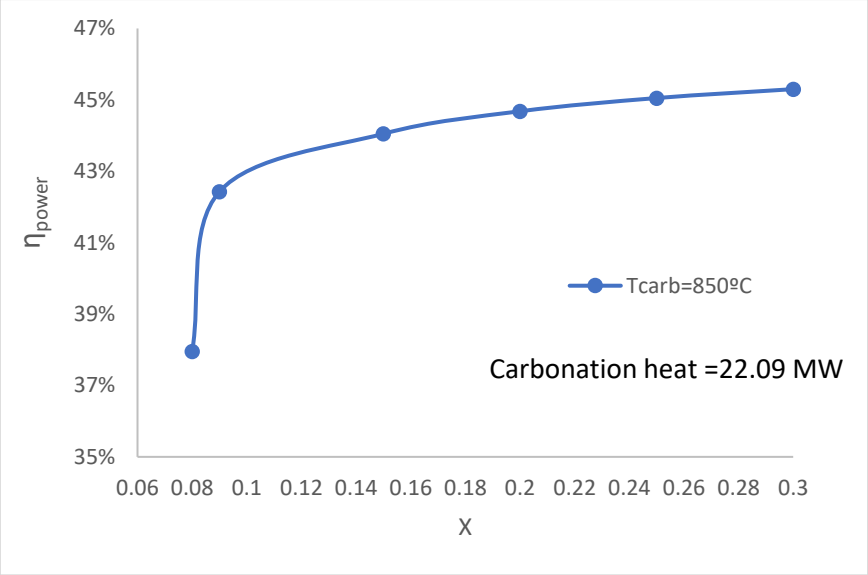

Figure 9. Variation of carbonator side efficiency as a function of CaO conversion (X)

As can be seen in **Figure 9**, the power production efficiency notably decreases for values of CO_2 conversion lower than X=0.1, being the limit for power production around X=0.07. It is important to remark that CaO conversion highly depends of calcination-carbonation conditions imposed. Conversion of limestone decays significantly after a few cycles at CaL conditions for CO2 capture and converges towards a residual value of just around 0.07-0.08 [13], [14]. Nevertheless, CaL conditions for TCES in CSP may be different to those employed for CO2 capture and CaO conversion could vary between X=0.1-0.5 [15]–[17].

Main consideration of the High-Temperature Direct (LT-D) scheme

- *This scheme presents an energy-optimized configuration which allows heat up the reactants to the carbonation temperature. Thus, solids can be stored at low temperature, increasing storage time as much as necessary.*
- *Optimized thermal integration of process streams allows a reduced extra cooling and heating requirements in the system. Cooling requirements are 0.07 MW per MW of power released in the carbonation* $(\mathrm{MW_{carb}})$*, which can be provided by water or air at ambient temperature (minimum cooling set point of 40* ºC*).*
- *If carbonation conditions drive to a CaO conversion lower than X=0.07, no isothermal carbonator operation is possible by the HT-D process scheme.*
- *Solids (a mixture of* $CaCO_3$ *and CaO) exiting the carbonator side to the storage tank are at low-temperature, which involves a highly energy integration in the calciner side to bring the solids up to the calcination temperature. The higher the temperature of solids entering the calciner, the higher amount of solar energy that can be stored, since the heat requires to bring the solid up to the calciner temperature is reduced.*
- *The direct integration based on a high-temperature Brayton regenerative cycle allows a high-power production from the heat released in the carbonation, concretely a 44% the heat released in the exothermic reaction is converted to electric power.*
- *This process scheme involves a high amount of* CO_2 *recirculating by the closed Brayton cycle, in a similar way that in the HT-D case.*

1.2.2. Indirect integration

In this new scheme the carbonator side configuration at industrial scale considers low-temperature (**LT**) energy storage and indirect (**I**) integration of the power block through a heat exchanger that can be coupled with an externally heated power block (Rankine cycle, supercritical CO_2, Stirling, …). Accordingly, the scheme is divided in two well differentiated parts: the carbonator side scheme and the power cycle scheme, which are mutually dependent through a heat exchanger. **Figure 10** shows a scheme of the proposed LT-I configuration.

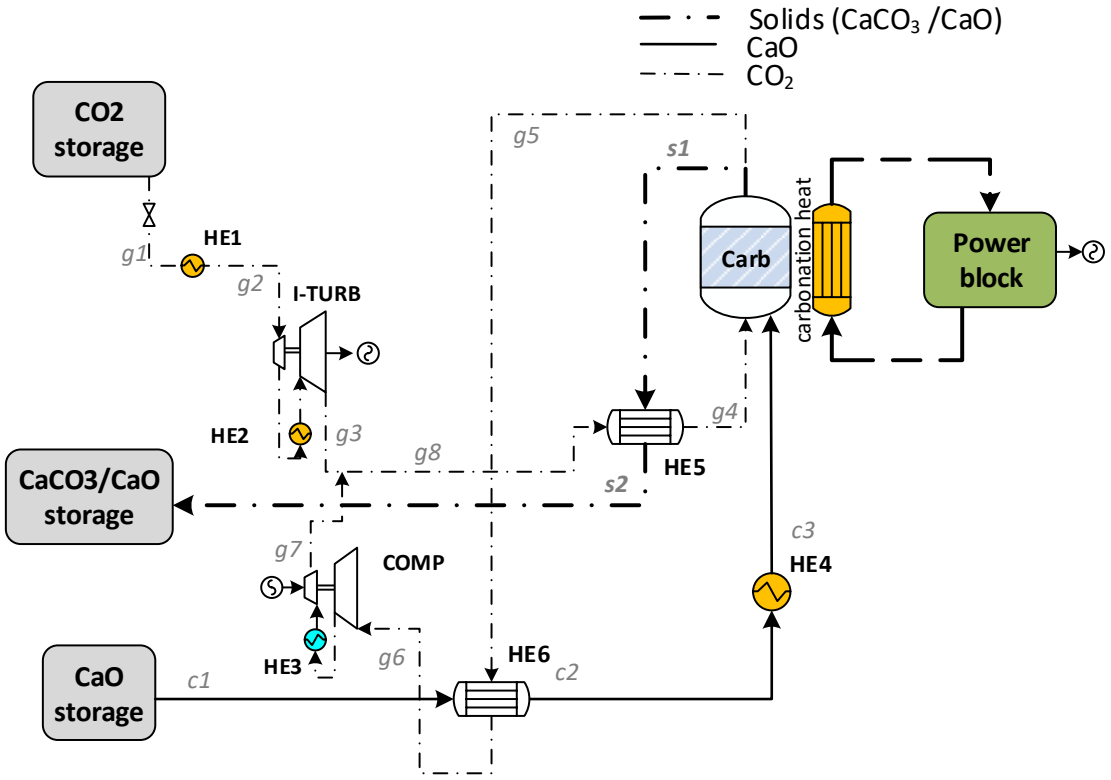

Figure 10. Low-temperature solids storage. Indirect integration. (LT-I) scheme

Following the same strategy than that proposed in the HT-I scheme, the CO_2 entering the carbonator is the stoichiometric value increased by 10% to ensure the correct fluidization of the solids in the reactor. The carbonation is carried out under atmospheric and isothermal conditions (850 ºC). This isothermal operation of the reactor by heating incoming cold streams from tanks up to carbonation temperature and extracting the exothermic heat from the reaction in a heat exchanger which delivers the thermal power to the power block.

This carbonation side scheme produces a small flow of hot CO_2 exiting the carbonator and the capacity for solids be preheating by this stream is very reduced in the LT-D scheme. This situation makes necessary the consumption of utilities to provide this extra heating power necessary to increase CaO temperature, requited to enable carbonation under isothermal condition (HE-4 in Figure 10). Otherwise the heat delivered in the reaction would not be enough to transfer the sensible heat to the incoming stream and therefore transferring thermal power to the power block. As in the case of HT-I configuration, it is important to take into account that some heat could be provided by integrating in the solids heating process any hot power cycle streams (i.e. steam turbine extractions for heating).

Table 9 and **Table 10** show the main equipment used in the LT-D scheme and the process simulation results respectively. Note that HE6 heat exchanger could not be interesting from an economic perspective due to the reduced amount of CO_2 flow exiting the carbonator, and the very reduced thermal power for heating.

Table 9. LT-I scheme (Figure 10) equipment description

Equipment	Type	Description
BLOWER	Electrical	The blower is required to overcome the pressure drop of the CO_2 circulating throughout the heat exchangers network. *In this scheme the carbonation unit operates at ambient pressure, thus the compressor included in the direct integration scheme has been replaced by a blower.*
HE1	Heater	This heater is required to increase the inlet turbine temperature from ambient value to 130ºC of set point.
HE2	Heater	This heater is required by the inter-heated turbine (I-TURB) to provide the require heat to increase the inlet temperate of the CO2 stream at each stage of the turbine
HE3	Cooler	
HE4	Heater	This heater is required to increase the enthalpy of cold CaO stream. This heater is required to enable carbonation.
HE5	Solid-gas heat exchanger	HE5 integrates both, hot solids stream and cold CO2 streams by cooling down the hot stream (much lower than the hot one) previously to storage, heating up the cold CO2 stream before entering the carbonator
HE6	Solid-gas heat exchanger	This heat exchanger enables to preheat the CaO stream existing the cold tank before entering the heater H4
I-TURB	Intermediate CO_2 turbine	Inter-heated turbine to reduce the pressure of the CO2 stream from CO2 tank (*supercritical conditions: 75bar and ambient pressure*) to carbonation pressure.
Carbonator	Isothermal	1 bar and 850 ºC.

The scheme represented in **Figure 10** has been simulated in ASPEN PLUS. Main results are included in **Table 10:**

Table 10. Carbonator side LT-I integration scheme. Main results

Stream results							
Stream	P [bar]	T [ºC]	m [kg/s]	Stream	P [bar]	T [ºC]	m [kg/s]
g1	75,00	25	5,6506	g8	1,1	23,1054	6,2157
g2	74,25	130	5,6506	c1	1	25	48
g3	1,1	21,3952	5,6506	c2	1	37,043	48
g4	1,07	835	6,2157	c3	1	700	48
g5	1	850	0,5605	s1	1	850	53,65
g6	1	40	0,5605	s2	0,97	749,227	53,65
g7	1,1	40	0,5605				
Heat exchangers thermal power							

ID	Heating [MW]	Cooling [MW]
HE-1 (Heater)	1,5904	-
HE-2 (TURB)	0,7551	-
HE-3 (COMP)		-0,0037
HE-4 (Heater)	29,1484	
HE-5 (HEN)	5,5649	-5,5649
HE-6 (HEN)	0,5084	-0,5084
Electric power		
ID	Consumption [MW]	Generation [MW]
COMP	0,0037	
I-TURB		-1,0217
Auxiliaries solids transport	0,48	
Auxiliaries cooling	0	
Performance results		
Energy to preheat the carbonation reactants [MW]	7,77	
Energy released in the carbonator to the power cycle [MW]	14,92	
carbonation thermal power released [MW_{carb}]	22,09	
ETA_pow=Net electric power produced/carbonation thermal power released	0,33	
Cooling demand [MW/MW_{carb}]	0	
Heating demand [MW/MW_{carb}]	1,43	

Main consideration of the Low-Temperature Indirect (LT-I) scheme

- *This integration scheme makes possible to reduce cooling and heating requirements in the system; nevertheless, an extra heating power is necessary to enable carbonation due to the low temperature storage conditions. The net heating thermal power after integration of streams would be 1.43* $\mathrm{MW/MW_{carb}}$.
- *The indirect integration allows a high-power production from the heat released in the carbonation, a 33% the heat released in the exothermic reaction is converted to electric power. The higher temperature of solids entering the carbonator the higher amount of electric power production. It is considered that the thermal efficiency of the power block is 45%.*
- *This scheme allows operation at ambient pressure in the carbonator, which makes easier the operation of the reactor.*

- Note that HE6 heat exchanger could not be of interest from an economic perspective due to the reduced amount of CO_2 exiting the carbonator, and the associated small amount of thermal power for heating.

1.3. Discussion of results

The schemes proposed along sections 1.1 and 1.2 have been simulated to analyse the heat released in the carbonation available for the power cycle.

Both high temperature schemes, the **HT-D and HT-I, allow the direct supply of the CaO stream into the carbonator** due to the high temperature of stored CaO. This is one of main advantages of this high temperature storage in comparison with **low-temperature schemes, which require more complex gas-solid heat exchanger network (LT-D) or extra heaters (LT-I)** to enable carbonation, otherwise the reaction heat would not be sufficient to heat up reactants to carbonation temperature. On the other hand, they deal with the challenge of high temperature storage of reactants and a capacity of storage for shorter periods of time.

LT-I scheme includes the heater HE-4 to heat up CaO stream, reducing the sensible heat to be transfer from exothermic reactor and therefore increasing the thermal power transferred to the power block. The base configuration considers that solids are heat up to 700ºC (out temperature), which involves a heating demand of 1.43 $MW/MWcarb$. Under this scheme the heater is necessary to guarantee carbonation and the minimum heating power to be released in the 0,76 $MW/MWcarb$ to heat up solids to a minimun temperature of 375ºC.

Global results have been obtained by considering CaO storage at 700ºC and a CaO conversion of X=0.15, which results in a CaO stream of 48 kg/s to release in the carbonation 22 MWth of thermal power. In the HT-D scheme, 7.77 MWth of the total thermal power released in carbonation are transferred as **sensible heat to preheat carbonation reactants** (96.55 kg/s of CO2 at 725.86 ºC and 48kg/s of CaO at 700 ºC), while in the HT-I scheme, 7.17 MWth are transferred as sensible heat (6.22 kg/s of CO2 at 835 ºC and 4 8kg/s of CaO at 700 ºC). By keeping constant the energy released in carbonator, the sensible heat required to preheat carbonation reactants increases when the CaO conversion is reduced and also when the storage temperature of CaO decreases. In this sense, sensibility analyses have been done for both high temperature schemes to determine the minimum storage temperature that would enable the carbonation. Thus,

Table *11* shows the minimum CaO storage temperature to guarantee isothermal operation in the carbonator.

Table 11. Minimum CaO storage temperature to guarantee isothermal operation

	Configuration			
	HT-D		HT-I	
X	0.15	0.07	0.15	0.07
Minimum temperature [ºC]	***385***	***625***	***337.1***	***626.4***

The heat released in the exothermic reaction is converted to electric power ($\boldsymbol{\eta_{power}}$) with different efficiencies, as function of the integration, depending on the configuration selected. As shown in **Table 12,** similar efficiencies are achieved in low and high temperature storage configurations. For this, a more complex heat exchanger network is proposed in the low temperature schemes wit the aim of introducing the reactants at as high temperatures as possible in the reactor by taking advantage of the hot outlet streams. On the other hand, there is an important performance difference between direct and indirect schemes. In the last one, the power cycle efficiency is assumed to 45%, considering reference values of Rankine cycles.

Table 12. Minimum CaO storage temperature to guarantee isothermal operation

	Configuration			
	HT-D	HT-I	LT-D	LT-I
η_{power}	***0.45***	***0.33***	***0.44***	***0.33***

As the sensibility analyses reflect (HT-D and HT-I schemes), the higher temperature of the solids entering the calciner the higher amount of electric power production. Considering that solids are stored from calciner at a maximum of 950^{o}C, the maximum efficiency is obtained for this temperature of CaO stored. Maximum efficiencies for the analysed cycles are shown in **Table 13**.

Table 13. Minimum CaO storage temperature to guarantee isothermal operation

	HT-D	HT-I
η_{power}	***0.59***	***0.47***

1.4. Notes about the heat exchangers to be considered at industrial scale

In order to avoid potential losses of CO_2 to the atmosphere, the carbonator side schemes proposed are based on a CO_2 closed-loop. Thus, all the schemes consider a gas-gas heat exchanger as regenerator to preheat the CO_2 entering the carbonator. The higher temperature of CO_2 arriving at the carbonator the higher amount of carbonation energy used for power production, with the consequent increase in plant efficiency. However, in the case of indirect schemes, due the low amount of CO_2 exiting the carbonator, this gas-gas heat exchanger could not be of interest from an economic point of view.

Solid-gas preheaters allow to increase the CO_2 temperature entering the carbonator -from the storage in which CO2 is at low temperature- using heat from the CaCO3 particles exiting the fluidized bed reactor after carbonation. Gas–solid heat exchange can be carried out in either open or closed configurations. Direct contact within an open configuration is a well-known technology [18]. Solids heating could be performed in a suspension preheater where gas and solids enter into contact sequentially in risers and are separated by cyclones, as commonly used in cement plants for raw material preheating [19]. In suspension preheaters raw particles are maintained in suspension by the hot gas from the carbonator. Due to high level of maturity of this technology, it seems an adequate option to carry out both the $CaCO_3$ particles cooling in the carbonator side.

In the case of the CSP-CaL integration in which CaO particles are preheated before entering the carbonator with the CO2 exhaust stream (see previous sections), an indirect gas-solid heat exchanger is needed in the carbonator side to avoid direct contact between CaO and CO_2, which could lead to partial carbonation with the consequent reduction in the carbonation heat transfer to the power cycle. Indirect solid gas heat exchange could be performed by using multiple heat transfer plates conveniently spaced to allow the flow of material to be heated inside [20]. Another high-temperature solid-gas heat exchanger was proposed by Al-Ansary et al. [21] in which particles circulate on the shell side through tubes arrangements while the CO2 passes inside the tubes. Moving packed-bed heat exchangers implementing shell-and-tube and finned shell-and-tube designs were investigated by Ho et al. [22].

2. CARBONATOR-POWER CYCLE INTEGRATION FOR THE SOCRATCES PROTOTYPE

This section analyses the carbonator-power cycle integration at SOCRACTES prototype scale (10 kWth in calciner). A model is proposed to estimate the heat transfer from the carbonator to the power cycle. The model combines a hydrodynamic simulation of particles inside the reactor with an energy model to estimate the heat removed by the working fluid to the Stirling engine.

According to the above, a fluidized bed reactor is considered as a first approach to estimate the carbonator-power cycle integration efficiency. From the carbonator model that is being developed within the task 2.2 (WP2), the carbonator-power cycle model proposed in this section will be updated with kinetics and hydrodynamics of the reactor to be built in SOCRATCES. This model update work will be developed within the task 2.3 (carbonator heat integration) and the updated information will be submitted in the deliverable *D2.3 Carbonator energy analysis.*

2.1. Starting point

Table 14 collects the main design and operating parameters initially considered as initial design conditions for SOCRTACES prototype.

Table 14. Initial consideration for the SOCRATCES prototype

CARBONATOR	
Type of reactor	Entrained flow reactor
Design temperature	750-850ºC
Design pressure	1-4 bar
Design thermal power	10 kWt
Design CaO flow rate	10-180 kg/h (*)
Design CO_2 flow rate	7-16 kg/h (*)
Preliminary reactor length	4 m
Preliminary reactor diameter	0.16 m
Median particle size, Dv (50)	1-100µm (**)
Heat transfer	Isothermal reactor
Heat exchanger	External Spiral
Auxiliaries	Electric heaters (10-12 kWe)
POWER CYCLE	
Type of power cycle	Stirling engine
Design maximum thermal power	10 kWt
Working fluid	$He/CO_2/N_2$

(*) Further information in section 2.2.
(**) More information can be found in deliverable D3.1

Regarding the carbonator temperature, operation in the range of 800-850ºC is considered sufficient to demonstrate the capacity for managing heat release at very high temperature

(higher than typical temperature of CaL for post-combustion temperature) while operation conditions are far enough from equilibrium temperature at ambient pressure or higher pressures. On the other hand, this temperature could be high enough to run the Stirling engine (albeit at a somewhat lower efficiency). From the second meeting of the project in Bremerhaven, it was proposed to operate the carbonator at isothermal conditions, keeping constant the temperature by using electric heaters in order to make independent the process, to assure stable operating conditions and to study on repeatable macro scale conditions the different phenomena involved in carbonator. After transfer heat to the Stirling engine (and depending on the final configuration with inclusion of additional auxiliaries as a chiller), the HTF should be recirculated to the carbonator at the higher temperature possible) in order to avoid freezing carbonation reaction in the reactor. If the Stirling operation requires that the HTF come back to the carbonator at low temperatures, the HFT could also be preheated in the carbonator by electric heaters.

Regarding the pressure range, carbonator will work at ambient pressure or at higher (e.g. 2-4 bar). For the Stirling engine, the pressure range in the HTF will be in the range of atmospheric pressure as it is an intermediate fluid that doesn't evolve through the engine. Engine´s manufacturer will indicate operating conditions.

The mass flow rate of CaO and CO_2 entering the carbonator depends on several variables as:

i) the maximum CaO conversion allowed (which is a function of the number of calcination-carbonation cycles). In spite of the SOCRATCES carbonator model has not been completed yet, previous works shows that after a few cycles the CaO conversion (X) converges to a residual value of around X=0.15 by using limestone as CaO precursor. The higher CaO conversion, the lower amount of solids to be introduced in the carbonator to produce a certain amount of thermal power. Thus, carbonator side operation could be designed for the worst case (X=0.15) to size the carbonator side equipments (valves, reactor, pipes) at the maximum solids flow. For the first calcination-carbonation cycle, the reactants mass flow will be lower than at design point (see section 2.2 for further details). Fresh limestone can be added to the process if required to maintain flows within the required for adequate equipment operation. In order to analyse the process facing the scalability seems interesting analyse the multicycle capacity of releasing the stored heat. The CO_2 mass flow entering the reactor should be at least the stoichiometric. To facilitate the operation, an extra amount of CO_2 should be considered. In the base case simulation (section 2.2), a CO_2 mass flow in excess of 10% has been proposed.

ii) the temperature of streams exiting the storage vessels. Depending on the number of storage hours, solids and CO_2 tanks isolation, CO_2 and CaO could be introduced at high temperature with a reduced support of the electric heater in the furnace.

iii) pattern of use of the electric furnaces and the carbonation thermal power at the design point. According to the Grant Agreement, 10 kWth in the calciner will be obtained. Thermal power production from carbonation is set taking into account this condition, and as with the design is expected a higher thermal power at calciner the design point of 10 kWth will be considered, with operation condition in the range between 2-10 kW. In continuous operation, this thermal power should be enough to preheat the reactants and release energy to the power cycle.

2.2. Integration scheme for SOCRATCES prototype

Figure 11 shows the preliminary design scheme of the carbonator reactor and the integration with the Stirling engine, as proposed by CERTH in the second project meeting in Bremerhaven. The reactor, which is divided in two sections, is kept at constant temperature by means of electrically heated furnaces. Hot CaO is introduced from the top of the reactor as a free flow. The CaO vessel (at the storage step) can be kept at the desired temperature by an electric furnace. This installation allows to heat or not to heat the tank (hot CaO would lose temperature depending on the insulation) and integrate an electric furnace for the solids going to the carbonator. This installation would allow to study the different effects on materials behavior and reaction. The CO_2 is also introduced hot from the top of the reactor to follow a co-current flow with particles, being previously preheated by the carbonation heat/electric furnaces. The solids exit the reactor at the bottom and are collected in the vessel downwards of the reactor.

Heat of reaction can be exploited by a working fluid (i.e. CO_2, Air, N_2or He) running inside a spiral that encircle the reactor and remove the produced heat.

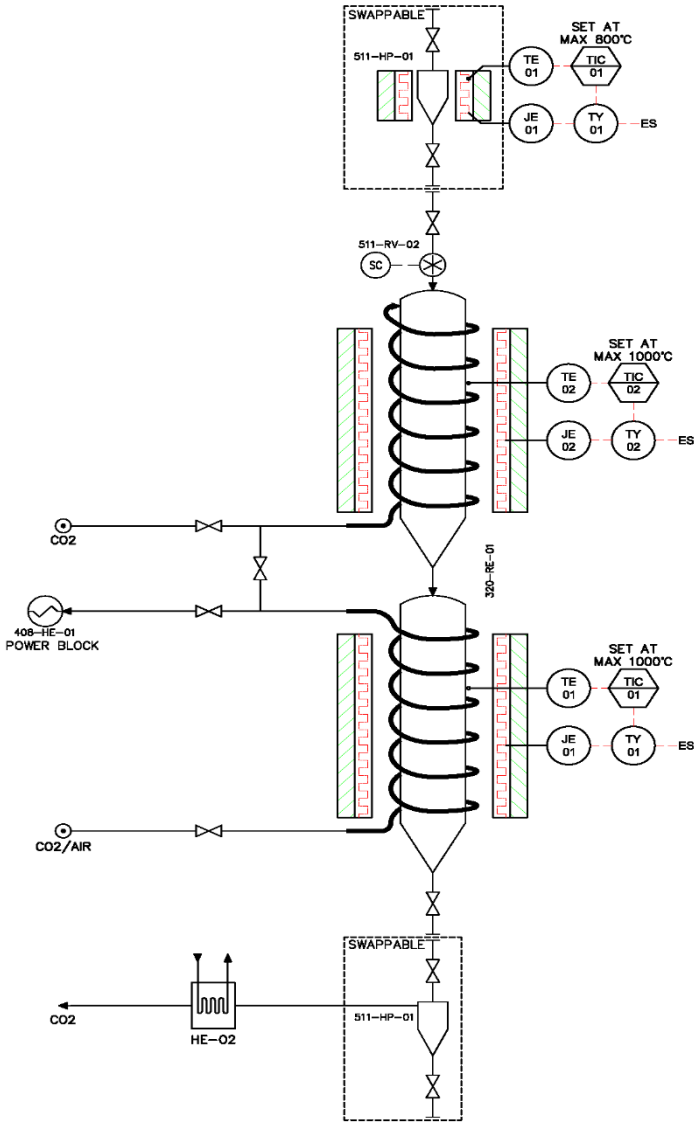

Figure 11. Indirect integration scheme – SOCRATCES prototype. Preliminary design scheme of the carbonator reactor (figure developed by CERTH)

The proposed carbonator-power cycle integration for SOCRATCES prototype has been simulated at stationary regime in ASPEN PLUS to estimate as first the mass and energy balances. **Figure 12** shows the process flowsheet. CO_2 is considered to be stored under pressure and an expansion valve is considered to reduce the pressure to match the carbonator one (atmospheric or not). Electric heaters for CaO and CO_2 are considered to bring the reactant to the carbonator temperature, fix in this simulation **at 800ºC**. CaO mass flow entering the carbonator is calculated in the base case to produce **10 kWth of carbonation thermal power**. CO2 mass flow is assumed to be **10% higher than the stochiometric amount**. As can be seen, the thermal power available for the power cycle is calculated as the carbonation thermal power produced less the thermal power needed to preheat the reactants.

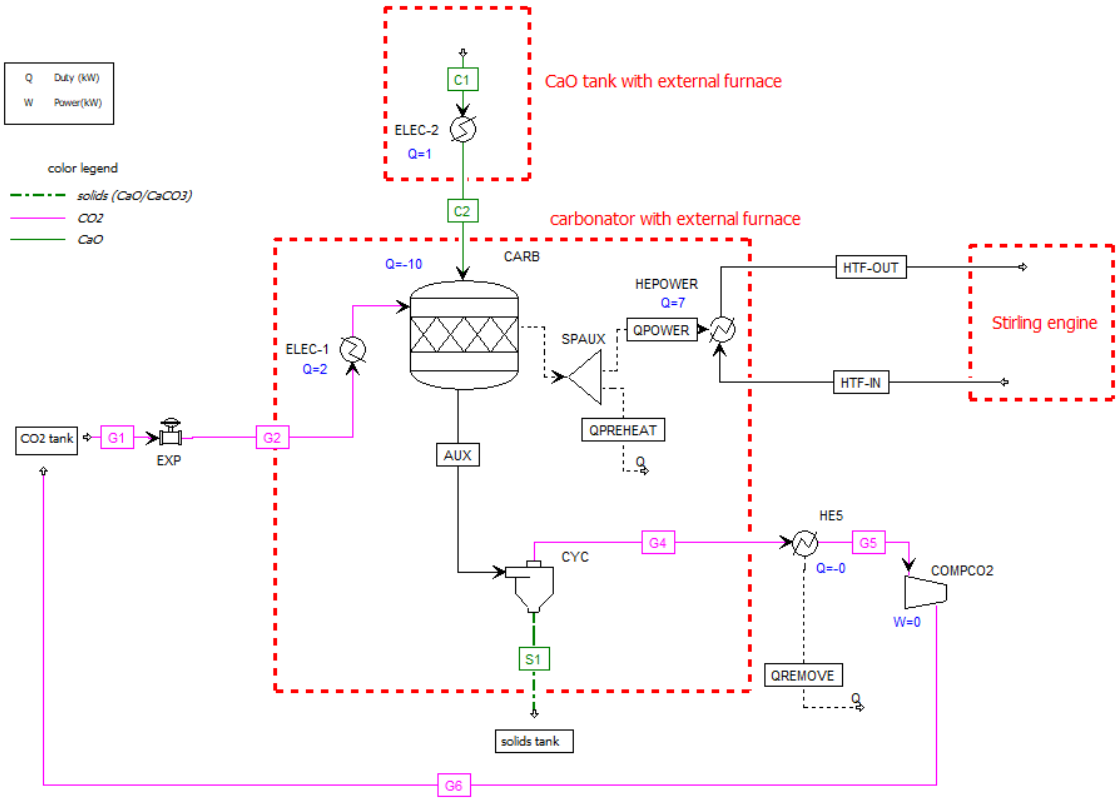

Figure 12. Carbonator-power cycle for SOCRATCES prototype. Aspen simulation flowsheet.

As previously indicated, fixing the carbonator power to 10 kWth, the mass flow of CO_2 entering the system depends on the CaO conversion, which depends on both reactions result (how is produced the reaction) and the number of cycles. **Figure 13** shows the minimum CaO mass flow to be introduced in the carbonation for releasing 10 kWth.

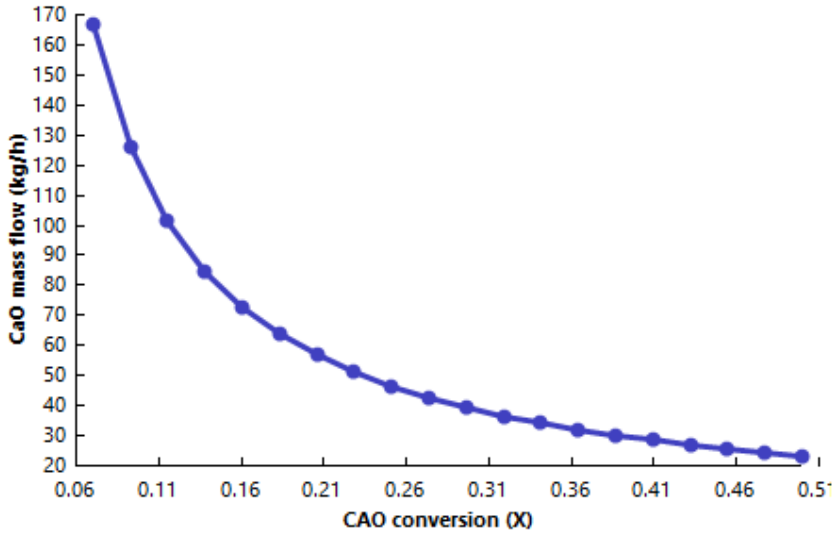

Figure 13. CaO mass flow to the carbonator to achieve 10 kWt released in the carbonation as a function of CaO conversion in the carbonator

On the other hand, the CaO storage temperature (for these simulations it is considered that CO_2 is stored at ambient temperature) affects to the thermal power available for electric power production in stationary regime, since in these simulations consider that the carbonation heat is enough to preheat the reactants (the external furnaces would be used for startup and control purposes). As previously detected in section 1, there is a minimum CaO supply temperature from which the heat needed to preheat the reactants is higher than the carbonation thermal power released, and therefore the isothermal operation of the carbonation is not possible (in this case electric furnace would provide the power for the power cycle). **Figure 14** shows the maximum thermal power (without considering thermal losses) provided to the HTF as a function of CaO supply temperature. As can be seen in **Figure 14**, if CaO storage temperature is lower than 430ºC, electric heaters should provide heat to operate the power cycle since carbonation heat release is not high enough to preheat the reactants. Considering that solids entering to the stored tank at 950ºC (the calcination temperature), the higher isolation of the solids storage tank, the higher number of hours that would be possible to run the carbonator for power production (at temperatures higher than 430ºC) without additional heating support.

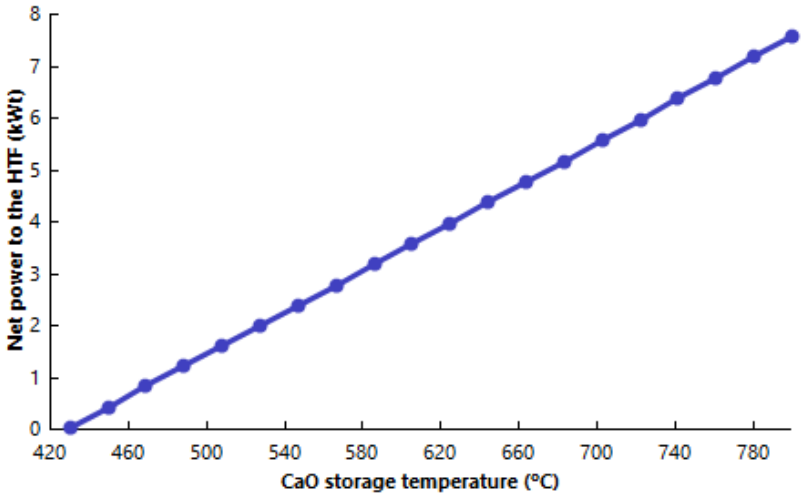

Figure 14. CaO mass flow to the carbonator to achieve 10 kWt released in the carbonation as a function of CaO conversion in the carbonator

Further details of power cycle integration will be obtained within the following tasks (WP4):

- *task 4.2 ("Power cycle modelling and design")*
- *task 4.3 ("Improving power cycle efficiency")*
- *task 4.4 ("Power cycle. Approach to prototype engineering and construction")*

2.3. System design model

The system design model aims at determining the expected efficiency of the Stirling engine when combined with the carbonator through an indirect coupling. This basically involves the following steps:

1) Modelling the carbonation reaction to calculate the CaO conversion and therefore the thermal power released by the exothermic reaction.
2) Calculation of the heat flux between carbonator and the heat transfer fluid and its temperature
3) Calculation of the Stirling efficiency

The full model has been implemented in Matlab. The structure of the numerical model adopted for the heat transfer calculation in the carbonator is shown in the next figure. This is mainly composed of two parts: the hydrodynamic model of the fluidized bed and the energy model for heat transfer analysis.

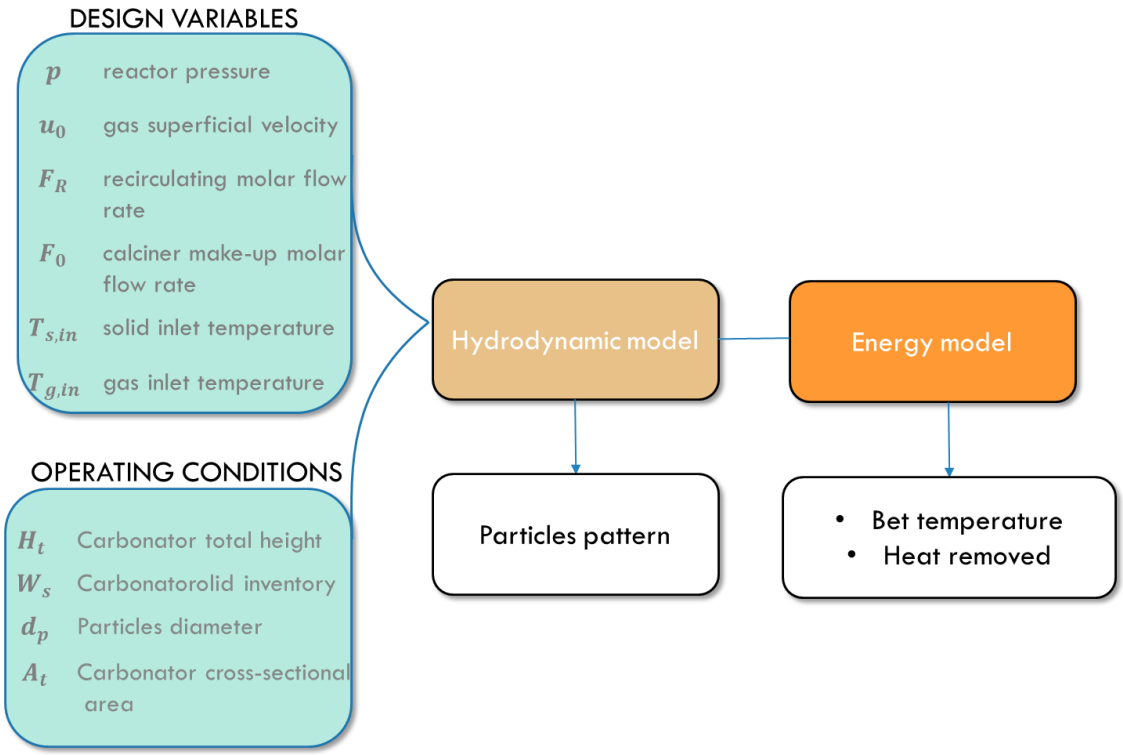

Figure 15. Structure of the carbonator model

The hydrodynamic model is taken from the work by Kunii and Levenspiel [23]–[25]. This model assumes that there is a dense region with constant solid volumetric fraction (f_d) and a lean region, where the volumetric fraction f_l reduces exponentially:

$$f_l = f^* + (f_d - f^*) \cdot \exp(-\alpha \cdot z_l) \quad (1)$$

where z_l is the coordinate in the lean region, f_d is the average solid volumetric fraction in the dense region, f^* is the limit value of volumetric fraction in the lean region and α is the experimentally calculated decay constant related to the exchange of particles between the upflowing and downflowing clumps.

The solid fraction given by equation (1) is used in order to obtain the solid inventory W_s, which is calculated considering the volumetric fractions in the dense and lean regions ([24]), namely:

$$W_s = A_t \cdot \rho_s \cdot H_d \cdot f_d + A_t \cdot \rho_s \cdot H_l \cdot \overline{f_l} \tag{2}$$

where A_t is the reactor cross section, ρ_s is the solid density, H_d is the height of the dense region, H_l is the height of the lean region and $\overline{f_l}$ is the average solid fraction in the lean region.

The particles are considered to move upward in the core region, and downward in the region near the wall. To model this flow, the so-called core/annulus model can be considered. This assumes a central core region, with few particles dispersed in the gas flow, and a wall region with large solid concentration. The same values of solid volumetric fraction are assumed in the core and in the annulus.

To predict the reactor temperature and the heat flux exchanged with the heat transfer fluid, the heat transfer coefficient between bed and surfaces should be calculated. This term considers three different contributions: particle convection, gas convection and radiation.

The first term is evaluated using a cluster renewal model [26]. This is based on two assumptions: 1) the temperature in the core region is uniform [27] and can slightly decrease near the wall, where heat transfer occurs; 2) clusters are exchanged between the core region to the annulus through a radial diffusion process. In the annulus, clusters flow and then disintegrate. The clusters reduce their temperature because of heat transfer, on the basis of the contact time.

The average heat transfer coefficient during contact time is obtained as:

$$h_c = \sqrt{\frac{4 \cdot k_c \cdot \rho_c \cdot c_c}{\pi \cdot t_c}} \tag{3}$$

Where the cluster specific heat (c_c), density (ρ_c) and thermal conductivity (k_c) are calculated as:

$$c_c = (1 - \epsilon_c) c_p + \epsilon_c c_g \tag{4}$$

$$\rho_c = (1 - \epsilon_c) \rho_p + \epsilon_c \rho_g \tag{5}$$

$$k_c = k_g \left(1 + \frac{(1-\epsilon_c)\left(1 - \frac{k_p}{k_g}\right)}{\frac{k_g}{k_p} + 0.28 \epsilon_c^{\,0.63 \left(k_p / k_g \right)^{0.18}}} \right) \tag{6}$$

and the contact time of the cluster t_c is obtained as the function of the contact length and the cluster velocity:

$$t_c = \frac{L_c}{U_c} \tag{7}$$

The cluster velocity obtained experimentally by Wu and co-workers [28] is 1.26 m/s.

Besides the thermal resistance of the particle convection, there is a gas film resistance on the wall, due to an almost particle-free zone which increases if the particles are coarser. This

resistance can be considered acting in series to the particle convection resistance [29]. It is expressed using the gas thermal conductivity and the dimensionless, experimental, gas layer thickness δ.

$$h_w = \frac{k_g}{d_p \cdot \delta} \tag{8}$$

The particle convection heat transfer coefficient is expressed as the series of the resistances, cluster thermal resistance and wall contact resistance:

$$h_p = \frac{1}{\frac{1}{h_c}+\frac{1}{h_w}} \tag{9}$$

When the surface is not covered by clusters, it is exposed to a dilute solid-gas phase, where the first heat transfer mechanism is the contact of the wall by the gas, which is almost at the bed temperature [30]. In [31] was proposed the following correlation:

$$h_g = \frac{k_g c_{p,p}}{d_p c_{p,g}} \left(\frac{\rho_d}{\rho_p}\right)^{0.3} \left(\frac{{u_t}^2}{g d_p}\right)^{0.21} Pr \tag{10}$$

where ρ_d is the dilute phase density that depends on the solids fraction in the dispersed phase.

At high bed temperature, radiation heat transfer from the bed to the wall becomes to be relevant. As also proposed in [32], the radiation heat transfer can be modelled considering the wall, the dense and the dilute phases as grey parallel surfaces. The radiation heat transfer coefficient can be calculate for the two phases as:

$$h_{rc} = \frac{\sigma(T_b^4 - T_w^4)}{\left[\frac{1}{e_c}+\frac{1}{e_w}-1\right](T_b - T_w)} \tag{11}$$

$$h_{rd} = \frac{\sigma(T_b^4 - T_w^4)}{\left[\frac{1}{e_d}+\frac{1}{e_w}-1\right](T_b - T_w)} \tag{12}$$

where the cluster emissivity can be calculate using the relation proposed by Grace:

$$e_c = 0.51(1 + e_p) \tag{13}$$

where e_p is the emissivity of the particles. About the emissivity of the dilute phase, it can be calculated using the relation given by Brewster (1986):

$$e_d = \sqrt{\frac{e_p}{(1-e_p)B}\left[\frac{e_p}{(1-e_p)B} + 2\right]} - \frac{e_p}{(1-e_p)B} \tag{14}$$

where B is 0.5 in case of isotropic scattering. All this heat transfer coefficients, particle convection, gas convection and radiation are then combined using the fraction wall coverage, the ratio of wall surface covered by the cluster, which is related to the cross-sectional averaged solid suspension thanks to experimental equation by Lint and Glicksmann (1994):

$$f = 3.5(1 + \epsilon)^{0.37} \tag{15}$$

Thus, the final heat transfer coefficient is:

$$h = f\left(h_p + h_{rc}\right) + (1 - f)(h_g + h_{rd}) \tag{16}$$

The model of the Stirling engine is derived from [33]. This model has been used in order to obtain the engine efficiency as the function of the gas temperature as well as the cold source temperature. As the model is theoretical, the calculated efficiency has been multiplied times a constant in order to match with the nominal efficiency of a commercial engine. The following

figure shows the engine efficiency as the function of the hot gas temperature and for three values of the cold reservoir.

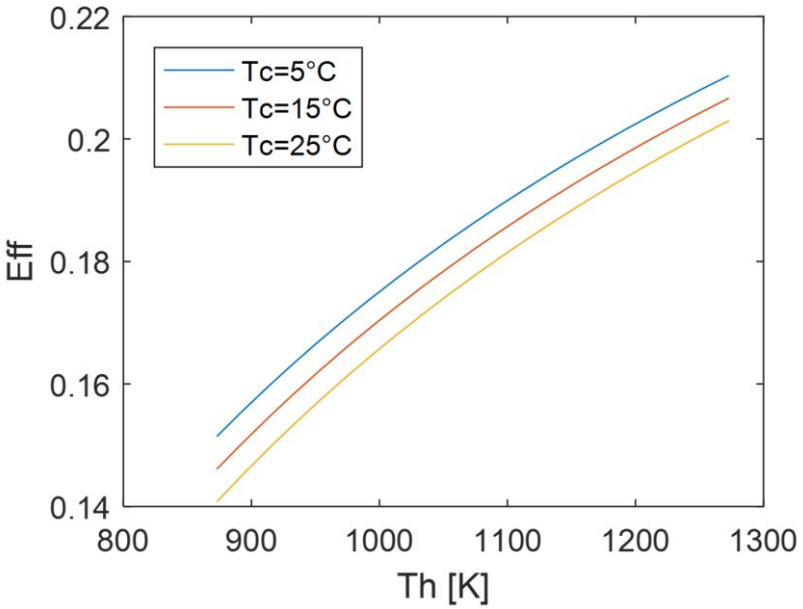

Figure 16. Stirling engine efficiency

The graph shows that nominal efficiency, at 900°C and 25°C for the hot and cold source respectively, can be obtained even in the case of a lower temperature of the hot source (e.g. 800°C), provided that the cold source is reduced of about 20°C. To achieve this result, an absorption chiller fed using the exhaust gases exiting the hot source heat exchanger.

2.4. Preliminary algorithm for optimum integration of the Stirling engine with the carbonator

The integration of the Stirling engine with the carbonator is to be achieved through a double heat-exchanger system that picks up the heat from the carbonator to release it to the Stirling engine's heater. The scheme has been shown pictorially in **Figure 17**. It has to be mentioned here that CO_2 has already been agreed upon as the choice of the heat-transfer fluid or the HTF upon the proposal from CERTH. Other options (e.g. air, N_2 or He) could be analysed during the project.

The required mass flow rate and static pressure of the blower can be calculated following the algorithm given below.

The pressure drop across the carbonator is a function of both the mass flow rate, the tube roughness, tube diameter and the temperature etc. Let us assume that the geometric and material definitions being constant this pressure drop can be written as

$$\Delta P_{carb} = g(\dot{m}, T_{in}) \tag{17}$$

The function is expected to be developed at a later phase by CERTH who are in charge of the carbonator design (task 2.2).

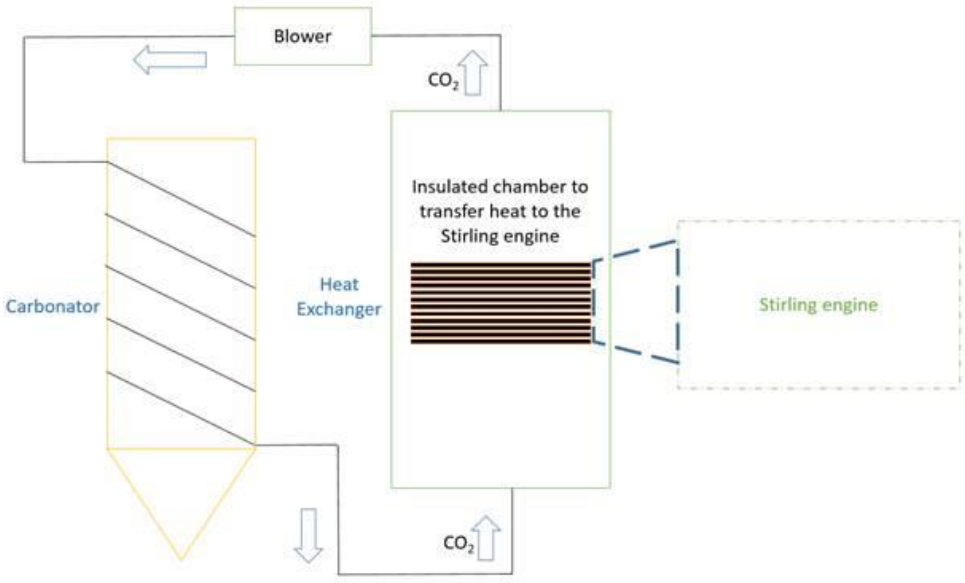

Figure 17: Pictorial representation of the scheme of integration between the carbonator and the power block

In a similar fashion, the outgoing temperature of the HTF from the carbonator can also be defined in the same fashion, recognizing that it also is dependent upon the mass flow rate and the incoming temperature. This gives us

$$T_{out} = h(\dot{m}, T_{in}) \tag{18}$$

It is expected that CERTH will provide equation 18 as well.

The thermal power transferred from the carbonator to the HTF is calculated using equation 19.

$$\dot{h} = \dot{m} \int_{T_{in}}^{T_{out}} c_p dT \tag{19}$$

The geometry of the heater is, at this point of the project, contemplated to be modified since some manufacturers (Microgen and Genoastirling) appear open to customization and it may be essential for the integration with the carbonator. Without the geometry of this heater finalized, it is not possible to determine an engineering estimate of the pressure drop across the heater or the overall heat transfer coefficient. However, it is certain that the function will have dependence on the outgoing temperature of the HTF from the carbonator and the mass flow rate. Therefore,

$$\dot{h}_{stirling} = j(T_{out}, \dot{m}) \tag{20}$$

Maximization of equation 20 under constraints will result in the optimization of the system, allowing the determination of the required mass flow rate.

The pressure drop across the insulated chamber for heat transfer to the Stirling engine can be determined using correlations available for common arrangements such as tube banks etc. However, in cases involving customized heat exchangers, it is better to involve CFD to estimate the pressure drop as a function of temperature and flow rate. TTZ will undertake this task in the future. Assuming the CFD yields equation 21, we can then estimate the pressure drop for the optimized mass flow rate found using equation 21.

$$\Delta P_{stirling} = k(\dot{m}, T_{out}) \tag{21}$$

Once functions *g* and *h* are received from CERTH, TTZ will commence its work to determine *j* and *k*, following which an optimum mass flow rate will be reported and the blower[1] will be specified. Curve fitting techniques can be liberally used if the functions are to be empirical nature, which they can be.

CONCLUSIONS

This document analyses the carbonation-power cycle integration from a process engineering point of view. Process schemes at industrial and prototype are analyzed and therefore this document provides useful information about the advantages, challenges, constraints and opportunities of the CSP-CaL integration under a wide range of operation conditions.

Regarding the SOCRATCES prototype, this work provides information about the carbonator-power cycle at this first stage of the project to answer some of the preliminary design issues to be addressed. Further useful information for the prototype construction will be collected within deliverables D2.1, D2.2, D2.3, D4.2, D4.3 and D4.4 in next months.

[1] Several manufacturers have agreed to customize their preexisting models to suit the requirements of the SOCRATCES HTF blower.

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