

CO₂ capture in cement plants by entrained flow reactors

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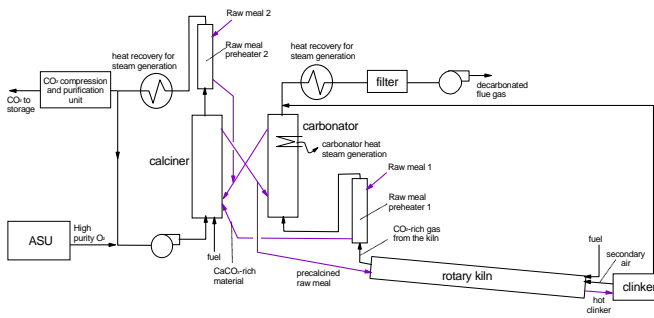
Abstract

Cement manufacturing process is extremely energy demanding and CO₂ emitting, and it represents the most promising industrial sector for capturing CO₂ via the Ca-looping process (CaL), which exploits the capability of calcium oxide (CaO, the main constituent of cement raw meal) to react with CO₂ forming calcium carbonate (CaCO₃) by means of an exothermic and high temperature reaction. In the framework of the H2020 CEMCAP project, two different process integration options of the CaL technology within a cement production process are being assessed, namely 'tail-end' and 'highly integrated' configurations. This study deals with a highly integrated configuration where the pre-calcliner of the cement plant is switched to oxy-combustion operation and the calcined material is fed to an entrained flow (EF) carbonator, where the residual CO₂ generated by combustion in the air-blown rotary kiln is captured. This integration option is assessed through process simulation, coupling a model of a complete cement kiln (developed in the Polimi's in-house code GS) with an EF carbonator reactor model (Matlab) and a Rankine steam cycle (Aspen Plus).

Integrated CaL model

The core idea of this configuration is switching the pre-calcliner of the cement plant to oxyfuel mode, so that it coincides with the calcliner of the CaL system. CO₂ generated in this reactor (from fuel combustion and raw meal calcination) is made available as concentrated CO₂ gas. The remaining CO₂ released in the air-blown rotary kiln (F_{CO₂}) from the additional fuel combustion and residual raw meal calcination is captured in the CaL EF carbonator. Before being introduced in the carbonator, the gas from the rotary kiln is fed to a two-stage raw meal preheater where a fraction of the raw meal is heated up before being fed to the calciner. This preheating section allows reducing the gas temperature and so decreasing the carbonator cooling duty. The remaining fraction of the raw meal is preheated in a parallel preheating tower (i.e. 'Raw meal preheater 2' in Figure), which is fed by the CO₂-rich gas leaving the oxyfuel calciner.

CO₂-lean gas at carbonator outlet is mixed with the exhaust air from the clinker cooler before being cooled in a heat recovery/steam generation section. A fraction of the calcined material exiting the calciner is sent to the rotary kiln, whereas the remaining material is used as sorbent in the EF carbonator.



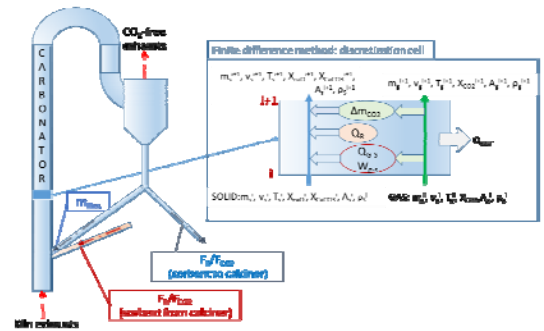
This system presents some differences from the conventional CaL technology based on CFB reactors:

- the calcined raw meal used for clinker production (composed by CaO but also by SiO₂, Al₂O₃, Fe₂O₃, MgO) constitutes the CaL sorbent;
- the sorbent particle size is lower (≈10-20 μm), which makes the adoption of entrained flow CaL reactors and their tight integration in the cement plant preheating tower the preferred option;
- the whole limestone flow rate fed to the cement kiln constitutes the sorbent make up (F₀), resulting in F₀/F_{CO₂} of about 4 that is two orders of magnitude higher than the values commonly considered in CaL.

EFR carbonator model

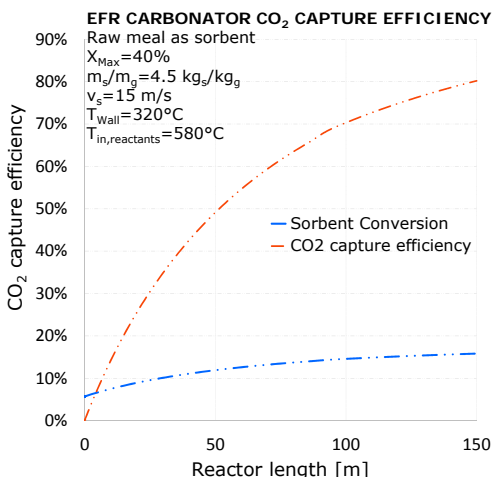
A simplified 1D steady-state model has been developed for the simulation of the EFR carbonator in Matlab. Main assumptions of the model are:

- Mass, energy and momentum balances solved along the axial direction for gaseous and solid phases (homogeneous characteristics along radial direction);
- Ideal gas behavior for the gaseous phase;
- Concentrated pressure losses considering the bending of the tube;
- Carbonation reaction controlled by reaction kinetics (i.e. mass transfer intra-particle resistances neglected);
- Constant temperature profile within the particles;
- Kinetic model proposed by Grasa et al. (2008) for natural limestones assumed, limiting maximum CaO conversion to 40% (uncertainty on possible side reactions: 2CaO+SiO₂→2CaO*SiO₂).



Grasa, J. C. Abanades, M. Alonso, B. González, "Reactivity of highly cycled particles of CaO in a carbonation/calcination loop," Chem. Eng. J., vol. 137, no. 3, pp. 561-567, Apr. 2008

Results



- A carbonator length of roughly 150 m is necessary to reach a significant CO₂ capture rate (CCR=80%), due to the high superficial velocity of this configuration (vs=15 m/s) that limits the reactants residence time and the sorbent conversion (i.e. max 15% achieved).

PERFORMANCE RESULTS

- Fuel input increase by 47% with respect to the reference plant without CO₂ capture;
- Significant gross electric power output by the heat recovery steam cycle (19.3 MW_{el} or 163 kWh/t_{clik}) that largely covers the additional auxiliary consumptions associated to ASU, CO₂ compression and additional fans;
- An electricity import of 164 kWh/t_{clik} remains, which is almost equivalent to that of the reference cement plant;
- Equivalent CO₂ emissions in this case are 200 kg/t_{clik}, 79% less than the reference case;
- A promising SPECCA index (2.32 MJ/kgCO₂) is reached due to the limited increase in the primary energy consumption.

CaL process results	Ref cement	EFR CaL
F ₀ /F _{CO₂}	--	4.1
F _{CaO} /F _{CO₂}	--	7.5
Carbonator CO ₂ capture efficiency [%]	--	80.0
Total fuel consumption [MJ _{LHV} /t _{clik}]	3223	4740
Rotary kiln burner fuel [MJ _{LHV} /t _{clik}]	1224	1180
Pre-calcliner fuel consumption [MJ _{LHV} /t _{clik}]	1999	3560
Electric balance [kWh_{el}/t_{clik}]		
Gross electricity production	--	163
ASU consumption	--	-73
CO ₂ compression	--	-111
Carbonator and calciner fans	--	-11
Cement plant auxiliaries	-132	-132
Net electric production	-132	-164
Direct CO ₂ emissions [kgCO ₂ /t _{clik}]	863.1	71.4
Indirect CO ₂ emissions [kgCO ₂ /t _{clik}]	105.2	128.7
Equivalent CO ₂ emissions [kgCO ₂ /t _{clik}]	968.3	200.1
Equivalent CO ₂ avoided [%]	--	79.3
SPECCA [MJ _{LHV} /kgCO ₂]	--	2.32