A NEW CO$_2$ CONCENTRATION PROCESS INTEGRATED INTO CEMENT PLANTS

Sébastien Wahl, PhD student, LGC Toulouse, France
sebastien.wahl@ensiacet.fr
Mehrdji Hemati, Professor, LGC Toulouse, France
Michel Gimenez, CO$_2$ and Industrial Innovation project director, LafargeHolcim, France

Key Words: CO$_2$ concentration, calciner, decarbonation, circulating fluidized beds.

Introduction

The worldwide CO$_2$ emissions of the cement industry are around 2 Gt/y. In order to mitigate these emissions and to reduce the carbon footprint, four main usual levers are utilized by the cement industry: the C/K ratio, representing the quantity of cement made over the quantity of clinker used, the burning of alternative fuels – including biomass, the improvement of the specific heat consumption of the cement kilns and CCS (CO$_2$ Capture & Storage).

Although very efficient because they can be applied in nearly all the cement plants all over the world, the first three levers are limited in many ways: the lack of cementitious additions in some locations, the limitation in fuel sourcing and the theoretical limit of the heat consumption of the cement kiln to some 1.8 GJ/tclinker. All of them being limited by the quality standard to be met by the cement in its applications. CCS is thus worth being studied for the cement industry to reduce its CO$_2$ footprint.

The capture technologies mainly serve to purify and concentrate the CO$_2$. Then the CO$_2$ is compressed and liquefied and is shipped to a storage location, either in a depleted oil or gas field, or in a deep saline aquifer. There exist several processes to separate the CO$_2$ from a gas mix.

The most developed, and only mature technology today, is the so-called CO$_2$ amine scrubbing technology (the amine solvent is the mono ethanol amine (MEA)). It has been extensively studied over the last 15 years and is in use for a long time into the fertilizer industry and into the gas industry.

This technology consists in scrubbing the CO$_2$ from the flue gas mix by an amine in an aqueous solution (e.g. $\approx 30\%$) and then to regenerate the solvent and release the CO$_2$ for compression, transport and storage. The solvent is then recycled to the scrubber.

Another technology in development today is the oxy-fuel process. This technology consists in burning the fuel in a mix of pure oxygen and recycled flue gas, rich in CO$_2$, thus concentrating the CO$_2$ in the exhaust gas of the plant.

The IEA (International Energy Agency) and the WBCSD (World Business Council for sustainable development), using ECRA (European Cement Research Academy) studies, have issued a “roadmap” report in 2009 [1], summarizing the technologies mentioned above and their potential interest to achieve the limitation of the global rise in temperature (2-3°C) between now and 2050. In December 2015, this limitation is confirmed since the main objective of the COP21 taking place in Paris consists in a limitation of 2°C.

Anyway, we can say that oxy-fuel technology is a first attempt to better integrate the CO$_2$ capture process into the cement plant as compared to the post combustion process.

The purpose of this article is to describe a new process to concentrate the CO$_2$ in a cement plant which has been developed by the authors. It is the result of collaboration between the INP Toulouse / Laboratory of Chemical Engineering and LafargeHolcim that started end of year 2011 (decarbonation process, M. HEMATI, M. GIMENEZ, PRO10045-12/05/011- with PCT extension / EP2012/058713, 2012). This new process is fully integrated to the clinker making process.

The technology consists in separating the calcination stage from the combustion process in the precalciner. We thus take advantage of the fact that more than 60 % of the CO$_2$ emitted by a cement plant is coming from the raw mix calcination.

The technology is based on the utilization of a heat exchanger comprising 2 fluidized beds, one where the combustion is taking place and another one where the calcination is taking place. Both fluidized beds utilize screened clinker nodules as heat exchange medium. This technology allows the complete separation of the combustion gases from the calcination CO$_2$.

The principle, shown on Figure 1, is based on a counter current heat exchange from clinker particles to raw mix particles. The clinker is separately heated up into a “combustor” and then circulated to the “calciner” where the CO$_2$ from calcination is released almost pure.

Moreover, the CO$_2$ flow produced is very hot ($T > 900\, ^{\circ}\mathrm{C}$) and it can be used to produce electrical power with a fairly high efficiency, which can lead to cement plant self sufficiency in the field of power (potential production of...
We expect that this electrical power production will lower significantly the cost of the CO2 capture. The usual Portland cement making process consists in a heat treatment of a raw mix approximately made of 80 % limestone and 20 % clay. The burning process temperature (i.e. the clinker sintering temperature) is roughly 1450 °C. Making a metric ton of Portland clinker is worth emitting ≈ 840 kg CO2/tclinker, where 540 kg/tclinker is coming from the calcination of the limestone and 300 kg/tclinker is coming from the combustion (where the specific heat consumption of the plant is roughly 3 GJ/tclinker). Therefore, 64 % of the CO2 emitted by a cement plant is coming from the sole raw mix calcination.

As already written above, this study concerns the development of a new CO2 capture process, integrated into the cement plant, taking advantage on the fact that the CO2 emitted in a cement plant does not come from the sole combustion of the fuel but mostly from the raw mix calcination stage. In a usual cement plant this calcination CO2 is mixed with the combustion gases thus leading to dilution. On the contrary here, we do not mix the two gases as can be seen on the following process scheme (Figure 1):

---

**Thermodynamic And Kinetic Analysis**

The raw material is mainly composed of solid calcium carbonate. In cement plants, the solid is decomposed into solid calcium oxide and gaseous carbon dioxide by thermal treatment. This endothermic decomposition is called decarbonation and represents the direct reaction of the reversible global reaction:

$$\text{CaCO}_3(s) + 180 \text{kJ/mol} = \text{CaO}(s) + \text{CO}_2(g)$$

As mentioned above, the main idea of the new process consists in the separation of the raw mix decarbonation and the combustion into two different units. Indeed, the circulating fluidized bed concept allows to isolate the CO2 emitted by the decarbonation from the fumes, gaseous products of the combustion. Thus, the gas atmosphere in the calciner is only composed of CO2. Consequently, the reaction equilibrium and kinetics are modified since the operating conditions in the new calciner differ from the ones in the conventional unit. These modifications need to be studied in order to validate the feasibility of the new process and eventually to take a step toward the sizing of the new units.

By minimizing the Gibbs energy calculated for this particular reaction at a given PCO2 and for a total pressure of P=1 bar, a unique temperature is found, the equilibrium temperature T\text{eq}. If the PCO2 in the unit is lower than the equilibrium value at a given temperature, the direct reaction, the decarbonation, is thermodynamically favored. Otherwise, the reverse reaction, the carbonation, is favored.

The CO2 partial pressure would be raised from about 0.3 bar (“combustion gaseous atmosphere”) to 1 bar (“pure CO2 atmosphere”) if the conventional calciner were replaced by the new one. Since only the direct
reaction is needed in this new process, a higher PCO\textsubscript{2} implies a higher temperature in the decarbonation unit. More than one equilibrium law has been presented in the literature thus, a range of temperatures that is define by comparing some of these laws restricts the temperature elevation needed in the new unit following thermodynamic considerations. Six laws are presented in Table 2 [2-6]. The temperature range goes from 897 to 920°C in order to keep the same “driving forces” (expressed as ΔP=\(P_{\text{eq}}(T)-\text{PCO}_2\)) as the ones calculated for the conventional unit for each equilibrium law. ΔP\textsubscript{1} represents the driving force for the conventional unit operating conditions whereas ΔP\textsubscript{2} is the one associated to the new calciner. The temperature elevation in the new unit would then be around 50 to 70 °C according to the thermodynamic analysis.

\[
\begin{array}{lcc}
\text{Conventional Calciner} & & \\
T (°C) & 850 \\
\text{PCO}_2 \text{ (bars)} & 0.3 \\
\text{P} \text{ (bar)} & 1 \\
\end{array}
\]

\textit{Table 1 – Conventional calciner operating parameters.}

\[
\begin{array}{ccc}
\text{Equilibrium laws} & T_{\text{equilibrium}}(°C) & T(\Delta P_1=\Delta P_2)(°C) \\
\text{[2]} & P_{\text{eq}} = 4,137.10^7 e^{\left(\frac{-170221}{RT}\right)} & 894 & 907 \\
\text{[3]} & P_{\text{eq}} = 1,01325e^{\left(17.74 -0.00108T+0.332 \ln(T) - \frac{22020}{T}\right)} & 896 & 907 \\
\text{[4]} & P_{\text{eq}} = 2,524.10^7 e^{\left(\frac{-168317}{RT}\right)} & 915 & 920 \\
\text{[5]} & P_{\text{eq}} = 1,850.10^7 e^{\left(\frac{-163620}{RT}\right)} & 903 & 913 \\
\text{[6]} & P_{\text{eq}} = 1,120.10^7 e^{\left(\frac{-159046}{RT}\right)} & 905 & 918 \\
\end{array}
\]

\textit{Table 2 – Equilibrium laws from top to bottom : [2-6]+law from LGC, and associated temperatures (°C) for PCO}_2/\text{Patm}=100\%.

Since the PCO\textsubscript{2} and the temperature of the new unit would have different values from the conventional reactor, it is necessary to study the kinetics of the direct reaction under the new operating conditions. Eventually, the evolution of the conversion rate of the decarbonation as a function of temperature, PCO\textsubscript{2} and the conversion rate itself need to be known. The objectives are the estimation of the new operating temperature according to kinetic considerations and the comprehension of the operating parameters influence on the direct reaction kinetics. Non-isothermal decarbonation tests were conducted in a TGA (thermogravimetric analyser) Q600 from TA Instruments to collect the necessary data for the study. Small amounts of pure solid CaCO\textsubscript{3} were heated from 20°C to 950°C under different gaseous atmospheres. The samples weighted 5mg, the inlet gas flow was equal to 100mL/min and the heating rate was 1°C/min.
The results of the non-isothermal tests are reported in Figure 2 where \( X \) is the conversion rate defined as:

\[
X = \frac{m_0 - m}{m_0 - m_f} \times 100, 
\]

- \( m_0 \) is the initial mass of solid \( \text{CaCO}_3 \),
- \( m \) is the sample mass at a given temperature,
- \( m_f \) its mass once the decarbonation is over
- \( T \) the temperature of the platinum bucket assumed to be the one of the sample.

Four different gaseous atmospheres were tested, from pure nitrogen (\( \text{PCO}_2/\text{Patm}=0\% \)) to pure \( \text{CO}_2 \) (\( \text{PCO}_2/\text{Patm}=100\% \)) with \( \text{Patm}=1\text{bar} \). Figure 2 shows that the higher \( \text{PCO}_2/\text{Patm} \) is the higher is the temperature at which the decarbonation starts. This observation is in agreement with the thermodynamic tendency highlighted above. However, this temperature appears to be higher than expected from the thermodynamic analysis. For example, if \( \text{PCO}_2/\text{Patm}=100\% \), the reaction begins for \( T=920^\circ\text{C} \) which is 5°C higher than the maximum value obtained from the law n°3 [4] in Table 2. Moreover, the temperature ranges between the beginning and the end of conversions may be converted to time ranges as the following assumption is made: \( \Delta t \beta = \Delta T \). Here, \( \Delta T = T(X=97\%) - T(X=3\%) \). The temperature ranges decrease as \( \text{PCO}_2/\text{Patm} \) increase which means that the conversion rates are faster for high ratios of \( \text{CO}_2 \) in the gaseous atmosphere (Figure 3) if the temperature is high enough for the reaction to begin. From these observations it may be conclude that the overall decarbonation rate under high \( \text{PCO}_2/\text{Patm} \) values is driven by thermal mechanisms. The inhibitor effect of \( \text{CO}_2 \) on the reaction is known, as well as the fact that increasing the temperature will make the conversion rate faster [7]. These data show that from a \( \text{PCO}_2/\text{Patm} \) value of only 5% the mass loss becomes way faster than under pure nitrogen atmosphere and that \( \Delta T \) decreases much slower between 5-100% than between 0-5%.

For \( \text{PCO}_2/\text{Patm} \) as low as 5% and above, the solid reactive only needs to reach a certain temperature to start its fast transformation.

Eventually, the temperature choice for the new unit is a compromise. On the one hand the mass loss needs to be fast in the new decarbonation unit and on the other hand a high temperature means a high operating cost. The temperature has then been chosen around 930°C for the process simulation. For this value, the temperature derivative of the conversion rate reaches a maximum. This choice needs to be confirmed by the kinetic study of the \( \text{CaCO}_3 \) decarbonation in fluidized bed.

An extended literature that deals with the decarbonation of calcium carbonate or limestone is available [7].

---

**Figure 2** – Conversion rate versus temperature for \( \text{PCO}_2/\text{Patm}=0,5,30 \) and 100%.

**Figure 3** – \( \Delta T \) as the range of temperatures from \( X=3\% \) to \( X=97\% \) versus \( \text{PCO}_2/\text{Patm} \).
Among these documents, a still large number presents results about the reaction under various PCO\textsubscript{2} atmospheres. However, fewer authors studied the decarbonation under a pure CO\textsubscript{2} atmosphere [2,8]. With the gain of interest for Ca-looping processes, some more recent studies complete the corpus [8]. If models from these documents are able to fit the data obtained from isothermal and non-isothermal tests of calcium carbonate decarbonation under pure nitrogen atmosphere [7,9], it appears much more complicated to find a function of operating parameters that describes well enough the evolution of the conversion rate with time under gaseous atmospheres with high values of PCO\textsubscript{2}/Patm.

It seems that the classical expression \( \frac{dx}{dt} = k(T)f(X)g(P_{CO_2}) \) used in the gas-solid kinetics field cannot represent the evolution of the conversion rate on a mathematical and a physical point of view at the same time [10]. This aspect will not be treated in detail in this document.

In a first attempt to model the mass loss of calcium carbonate under a pure CO\textsubscript{2} gas flow, an empirical model is presented here (Figure 4). This model is based on the following observations:

For each PCO\textsubscript{2}/Patm value, there is a linear expression that links \( P_{eq}(T) \) and \( X \) such as \( P_{eq} = a_iX + b_i \) where \( a_i \) and \( b_i \) vary with PCO\textsubscript{2}/Patm. Moreover, \( a_i \) and \( b_i \) have linear dependencies on PCO\textsubscript{2} such as \( a_i = k_1P_{CO_2} + k_2 \) and \( b_i = k_3P_{CO_2} + k_4 \).

By choosing the equilibrium law n\textsuperscript{6}, established in the LGC by performing simulations thanks to HSC Chemistry\textsuperscript{®} v5.1, from Table 2, \( P_{eq} \) can be replaced by its expression. It is then possible to obtain a function that links \( X \) to \( T \) and PCO\textsubscript{2}. In order for this model to be added in a simulation code, it should be written for three different temperature ranges:

- \( T<T_0 \) \[ X=0 ; \]
- \( T_0<T<T_1 \) \[ X = \frac{P_{eq} - k_3P_{CO_2} - k_4}{k_1P_{CO_2} + k_2} ; \quad k_1 = 3.3 \times 10^{-3} ; k_2 = 3.0 \times 10^{-4} ; k_3 = 1.9 ; k_4 = 3.0 \times 10^{-2} ; \]
- \( T_1<T \) \[ X=1. \]

By comparing the time derivative expression of the model to common formula cited in the literature for gas/solid reactions [9], it appears that its mathematical form cannot be identified. Whereas the empirical model is not satisfying enough on a kinetic study point of view, it could yet be very useful if the decarbonation conducted in fluidized bed show similar linear tendencies between \( P_{eq} \) and \( X \), and/or \( (a_i,b_i) \) and PCO\textsubscript{2}. Eventually, this simple model represents well the evolution of the conversion rate with temperature for a large range of PCO\textsubscript{2}/Patm.

**Figure 4** – Experimental conversion rates and empirical model results (continuous colored lines) versus \( T \) for PCO\textsubscript{2}/Patm=5,30,100%.

**Description Of The Process**

The principle of this technology, presented in Figure 1 and Figure 5, is based on the use of heat exchanger-fluidized bed reactors implementing: A heating zone where fuel (pet coke, natural gas, waste...) is burned in a combustor within a solid as a heat transfer media. The combustor may be a heat exchanger-reactor in dense fluidized bed or in a moving bed. The solid coolant, used for this application, is crushed clinker particles with a mean particles size between 400 to 1000 microns.

A heat transfer area where the heat transfer is done from the hot clinker media to the raw material. This is in this area, called “calciner”, where the decarbonation is taking place. It is an interchange-fluidized bed reactor
operated in counter-current between the hot medium (clinker) which is flowing down, while raw material and gas (mainly CO₂) are flowing up due to the difference in particle size distribution between the clinker and the raw mix. The clinker is more than 10 times coarser than the raw mix (35 µm).

This technology allows complete separation of the combustion flue gas, composed mainly of nitrogen and carbon dioxide, from the effluent gas of the decarbonation reaction, mostly composed of carbon dioxide. At calciner outlet, the temperature of the CO₂ is very high and allows the production of a high quantity of electrical power using a steam turbine whose advantages are:
- to lower the CO₂ temperature out of the calciner from 930°C down to 350°C. Part of this flow is diverted to the calciner and is used as fluidizing gas. The other part is sent to the storage location to lower the temperature of the gas out of the combustor from 1000 - 1100°C down to 800°C, avoiding the decarbonation of the raw mix to start into the pre-heater thus preventing to loose some CO₂ before the calciner stage thus enhancing the CO₂ capture ratio to produce a quantity of electrical power reaching plant self-sufficiency.

Process Simulation

The simulation of the process is based on the simultaneous processing of material and enthalpy balances established on the various elements of the process taking into account the thermal losses, false air flow and enthalpy of various reactions (decarbonation, combustion and sintering). The simulation program was initially validated on an existing plant.

The simulator was then changed to allow to consider a separate line decarbonation process, but also to test solutions to study energy integration and maximize the amount of CO₂ recovered through the decarbonation reaction. Indeed, the simple replacement of the precalciner by a combination of a calciner and a circulating fluidized bed combustor is resulting in a high decarbonation rate at calciner stage. However, to achieve this performance of the decarbonation, the operating conditions of the overall process are changed, especially the temperature of the gas available to preheat the raw mix. Thus, without making some design modifications, it is very difficult to avoid some decarbonation of the raw mix at the preheater stage.

Several solutions have been reviewed in order to reduce the gas temperature at the inlet of the preheater. The solution chosen is to recover energy with a heat exchanger placed at the combustor gas exit, and another one placed on the CO₂ stream out of the calciner (Figure 6). This solution reduces the temperature of the combustor flue gas and therefore the temperature of the raw mix out of the preheater. The presence of a sink term in the process (a power output) results in an increase of specific heat consumption of the cement kiln in the order of magnitude of 20 to 25% as compared to the non modified plant.

Energy recovery on flue gases and on the CO₂ can produce up to 140 kWh of electricity per tonne of clinker and thus reach plant power self-sufficiency.
Conclusion

This document has allowed us to describe a new technology to concentrate the CO$_2$ fully integrated into the cement plant. Until now, lab trials have been performed in the LGC laboratory in Toulouse where we have obtained kinetic and thermodynamic data allowing to validate the feasibility of the decarbonation under the new operating conditions and to make the energy and mass balances for this new process. Then, we have shown that the new process can be integrated into the cement plant and that the extra heat required getting pure CO$_2$ out from the calciner could be used to produce enough electrical power to assure plant self-sufficiency. We expect that the CO$_2$ capture using this process will be much less expensive than the "usual" technologies being considered today.

References


Figure 6 – Scheme of the clinker plant with the new units integrated.