

# Modeling of Carbonation and Calcination Reactions of Ca-Looping Process for CO<sub>2</sub> post-combustion capture in gPROMS®

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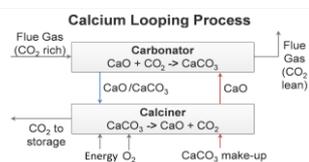


Figure 1. Schematic of Calcium Looping Process

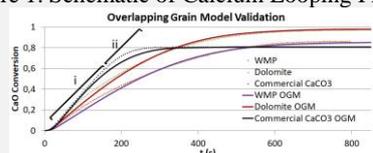


Figure 2. OGM validation for different sorbents. For Dolomite: i – Kinetic Regime, ii – Diffusional Regime;

## Introduction

Calcium-looping (CaL), is a post-combustion technique for carbon capture and storage (CCS), that relies on the carbonation reaction of CaO(s) to capture CO<sub>2</sub>(g), and on the calcination reaction of the resulting CaCO<sub>3</sub>(s), to generate a stream of highly concentrated CO<sub>2</sub>(g), effectively separating it from the stream of flue gases. The CaL process is a very promising candidate for industrial post-combustion CO<sub>2</sub> capture because widely available and low-cost natural limestone can be used as a sorbent; it is also a suitable process for retrofitting existing plants [1], lowering the overall cost and complexity of implementation.

The CaReCI – Carbon emissions Reduction in the Cement Industry – project, which includes the work here presented, aims to mitigate CO<sub>2</sub> emissions via cooperation with the Portuguese cement producer CIMPOR, to perform a techno-economic evaluation of the implementation of a CaL reactor in the producer's industrial plant. The CaL process is especially interesting when the cement industry is concerned, due to the possibility of using the deactivated sorbent from the CO<sub>2</sub> capture as feedstock for cement production [2].

## Objectives

The objective of the present work is to model the carbonation, the calcination reaction and corresponding pore dynamics using the gPROMS ModelBuilder® software. Both models are implemented and the OGM is validated for various sorbents, laying the groundwork for the simulation of sorbent deactivation along multiple cycles using the pore dynamics and the relation between loss of pore area and loss of sorbent reactivity.

## Methods

Two different models were used: the Overlapping Grain Model (OGM) [3] for the carbonation reaction and a modified version of A rate equation theory for the pore size distribution of calcined CaCO<sub>3</sub> (RThPSD) by P. T. Liang *et al.* [4]. A brief explanation of both models ensues, with emphasis on the changes done to the RThPSD.

### Overlapping Grain Model - Carbonation

The OGM is a grain model that considers each CaO particle to be comprised of solid and spherical grains randomly distributed throughout the particle. The formation of CaCO<sub>3</sub> during the reaction is assumed to happen at grain surface, causing the

In this work, the Overlapping Grain Model (OGM) [3] and A rate equation theory for the pore size distribution of calcined CaCO<sub>3</sub> (RThPSD) [4] were implemented in gPROMS® software. The OGM models the carbonation of CaO and the RThPSD the calcination of CaCO<sub>3</sub> and respective pore dynamics. The OGM was validated using data from fluidized bed reactor experiments, and accurately models the reaction regimes observed. The pore structure of the CaCO<sub>3</sub> particle was added as an initial condition to the RThPSD, and the calculation of surface area of vacancies was changed to avoid overestimating total pore area. The vacancy balance equation was also corrected to avoid undue pore volume disappearance. This work lays the basis for the simulation of sorbent deactivation in Ca-Looping by integration of both models, to be done after the validation of the modified RThPSD model.

grains' volume to expand concentrically, increasing the grains' radius, and shrinking the radius of the unreacted CaO core.

One characteristic of the carbonation reaction is that it exhibits two distinct main reaction regimes: a kinetic controlled profile for small reaction times, and a transitional and a diffusional regime for longer times [2]. Modeling the particle as an aggregate of dynamic grains with shells of CaCO<sub>3</sub> – allowing for particle porosity - adds two mechanisms that can control the rate of reaction besides the intrinsic chemical reaction. Particle porosity allows for the inclusion of the diffusion of CO<sub>2</sub> through the solid, and the layer of CaCO<sub>3</sub> around the grain adds an additional resistance to the transport of CO<sub>2</sub> between the pore and the reaction front. These two effects and the intrinsic reaction rate allow for a very accurate simulation of the carbonation reaction, and its two reaction regimes. The OGM, however, cannot estimate the maximum carbonation conversion, and uses an input parameter  $V_d$ , the deactivated fraction, to achieve the desired maximum conversion.

### A rate equation theory for the pore size distribution of calcined CaCO<sub>3</sub> – Calcination

The RThPSD models the calcination reaction with a shrinking core model, where a CaCO<sub>3</sub> core gives way to a shell of CaO. It also models the dynamics of the porous structure using a rate equation based on a balance to the number of vacancies of any given size. The RThPSD considers that two phenomena alter the porous structure during calcination: the release of CO<sub>2</sub> from the reaction, which creates vacancies by leaving the lattice; and the sintering process, which occurs naturally in CaO due to the high temperatures necessary for calcination.

The model, as presented in [4], has some shortcomings, for example, the lack of initial conditions for the rate equation derived from the experimental pore size distribution (PSD) of the initial unreacted CaCO<sub>3</sub>. Thus, the parameter values that result from model validation will not accurately represent the decomposition and sintering processes. The original model assumes that the particle is initially a solid with no porosity and that the porous structure present in the final PSD originates solely from the release of CO<sub>2</sub>, which is not true, due to CaCO<sub>3</sub> being porous [2]. The PSD after calcination is thus inextricably linked to the PSD of the original unreacted CaCO<sub>3</sub>. Our version of the model adds initial conditions, obtained by assuming that the experimentally measured porous volume for a given pore diameter is equivalent to the total volume of vacancies of the respective size, assuming these vacancies to be spherical.

Furthermore, in the original model, the authors calculate the total surface area of the vacancies in the particle as the surface area of a sphere. However, sorbents for CaL are typically analyzed using N<sub>2</sub> adsorption-desorption experiments in conjunction with the BJH model [3,5], where the assumption that pores are cylindrical, amongst others, leads to  $V_{pi} = D_{Avg} \cdot S_i / 0.04$  [6], a relationship between pore volume, average pore diameter and pore area. Since, for a sphere of volume  $V$  and radius  $r$ , the superficial area  $S$  is  $3V/r$ , assuming the vacancies as spherical when calculating their surface area will generate values exactly 150 times larger than when using the BJH equation. As total pore area plays a very important part in the reactivity of the sorbent [5], overestimating this property will skew future simulations towards less conservative values of conversion, which is not desired. In our version of the model, we assume the pore area to be correspondent to a cylinder with a total volume equal to the total volume of vacancies of a given diameter  $d_i$ ; and thus the pore area is calculated using the BJH equation presented previously.

Along these improvements, the pseudo steady-state approximation originally assumed for the CO<sub>2</sub> partial pressure has been forgone; and the balance has been modified to make the effects of CaCO<sub>3</sub> decomposition and CaO sintering simultaneous, instead of sequential. The vacancy balance was also changed to correct an error where the total volume of vacancies would decrease, which does not occur during calcination [4], as no pore straightening mechanism is present.

## Results

The OGM was validated using experimental data from a fluidized bed reactor experiments for three different sorbents: commercial CaCO<sub>3</sub>, dolomite, and waste marble powder (WMP), a residue from the Portuguese marble industry, recently shown to have economic potential as a sorbent by Pinheiro et al. [7]. As can be seen on the graphical abstract (Fig. 2), the OGM was fitted to the experimental results with a great degree of accuracy, being able to replicate both reaction regimes for the all sorbents, highlighted for the Dolomite series as line segments *i* and *ii*. A slight deviation exists for the commercial CaCO<sub>3</sub>, where the transition to the diffusional regime is sooner than expected. This can be related to the grain size distribution used to model the results for this sorbent, which was estimated using the experimental PSD as a basis. The relation between both is not straightforward, and it seems that a reallocation of the CaO volume present in higher grain sizes to lower sizes would benefit the fitting, as the CaO would be more easily available – CO<sub>2</sub> transport-wise – and thus the diffusion would only hinder the reaction rate for higher conversions.

As for the improved RThPSD model, it is still undergoing validation, since somewhat extensive experimental work is required. Notwithstanding, the changes made, especially the inclusion of initial conditions for the vacancy distribution, make the RThPSD apt to more realistically model the effects of

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calcination on the pore structure of a given sorbent and eventually estimate changes in pore area for different starting pore structures. The original model's lack of proper initial conditions for the vacancy distribution circumscribe it to single calcinations that result in PSD's with bimodal distributions (as can be seen on the *Results* section of [4]).

As for the correction made to the vacancy balance, simulations were ran using the values for the fitting parameters originally obtained in [4] using both the original balance and our modified version. The results for total vacancy volume along time for both simulations are plotted in the figure below.

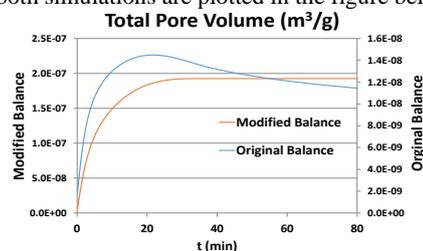


Figure 3. Total pore volume (m<sup>3</sup>/g) using the original and the modified vacancy balance.

For the original balance, not only is the total volume always below that of the modified version, as it can be observed that around 35 minutes, when the reaction terminates, the pore volume has been decreasing for approx. 10 min due to the vacancy generation not being enough to offset the artificial volume consumption in the original balance. When using the modified balance the volume is conserved, as expected.

## Conclusion

The implementation of OGM in the gPROMS ModelBuilder® software and subsequent validation with data from a fluidized bed reactor was successful, with the OGM being able to accurately replicate the experimental conversion profiles. The modified RThPSD model is yet to be validated, but several improvements were implemented in the same software, and simulations were made using values from the validation of the original model [4], which allowed verifying the improvements were correctly implemented. Seeing as the OGM cannot predict maximum CaO conversion, the relationship between loss of pore area and loss of sorbent reactivity is especially important and must be studied in order to be considered in the model. The improvements made to the RThPSD model will allow for the proper modeling of the changes to the pore structure during calcination which, upon validation, will make possible the estimation of loss of area for any given temperature, pressure and initial pore structure. The next step will be the validation of the improved RThPSD followed by the use of both models to estimate sorbent deactivation during cycling between carbonation and calcination reactions for various sorbents. The objective of the CaReCI project is to create a multi-scale model of a CaL process, where the models described in this work serve as particle-scale models.