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## Modelling Full Cycles of Carbonation-Calciation for Calcium Looping Process Simulation

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### Abstract

This work is part of a study to develop a multi-scale model of a Ca-looping (CaL) post-combustion process for CO<sub>2</sub> capture that relies on the carbonation reaction of CaO (s) and on the calcination of the resulting CaCO<sub>3</sub> (s) to generate a stream of highly concentrated CO<sub>2</sub> (g).

The literature lacks models that combine the modelling of both reactions with a cyclic structure that accounts for sorbent deactivation and allows for a realistic estimation in the case of incomplete reactions or different reaction media. Therefore, in this work two sub-models are combined to form this novel modelling approach for the simulation of complete carbonation-calciation cycles of the CaL process: The overlapping grain model for the carbonation reaction, and a proposed modified version (mRThPSD) of the rate equation theory for the pore size distribution (PSD) of calcined CaCO<sub>3</sub> (RThPSD) for the calcination.

The cyclic structure accounting for sorbent deactivation present in the proposed model was justified using data from fixed bed reactor experiments which highlights the relationship between loss of superficial area of CaO sorbents and loss of reactivity.

The model was implemented in gPROMS ModelBuilder<sup>®</sup> software and was validated with data from fixed bed reactor experiments for different CaL sorbents. One full CaL cycle was simulated successfully for dolomite, with the model estimating both reactions profiles and changes to the calcinated particle PSD with errors below 3%.

**Keywords:** Calcium-looping, CO<sub>2</sub> capture, modelling, carbonation, calciation.

### 1. Introduction

Calcium-looping (CaL) is a post-combustion technique for carbon capture and storage, where the carbonation of CaO (s) is used to capture CO<sub>2</sub> (g) and form CaCO<sub>3</sub> (s), the calcination of which yields a stream of highly concentrated CO<sub>2</sub> (g). CaL is a very

promising candidate for industrial post-combustion CO<sub>2</sub> capture due to the fact that widely available and low-cost natural limestone can be used as a sorbent.

Several carbonation and calcination reaction models can be found in literature, but one complete model that includes both reactions and a cyclic structure accounting for sorbent deactivation during reaction cycling does not exist. An existing model by Zhou et al. (2013) attempts a similar concept by combining the Overlapping Grain Model (OGM) by Liu and Dennis (2012) with an empirical equation that correlates sorbent deactivation with the cycle number. However, the lack of a detailed calcination model restricts it to the experimental conversion loss profile that originated the correlation, and respective temperatures and atmosphere compositions.

This work is part of a study aiming to techno-economically evaluate the implementation of a CaL CO<sub>2</sub> capture process in a Portuguese cement producer's industrial plant based on a multi-scale model of a CaL reactor. Hence there is an urgent need for a model of carbonation and calcination reaction cycles to be used for different reaction temperatures and reaction media, and thus different extents of reaction. By modeling the changes of the sorbent particle's porous structure during calcination using a modified version of the model originally proposed by Li et al. (2016), it is possible to estimate the changes on the sorbent particle's surface area during this reaction, which can be experimentally correlated to the loss of carbonation conversion. By estimating the post-calcination sorbent surface area, one can simulate the loss of carbonation conversion along multiple carbonation-calcination cycles for different extents of both reactions, as well as different temperatures and CO<sub>2</sub> partial pressures.

The objective of this work is to model the complete cycle: the carbonation reaction, the calcination reaction and the subsequent changes on the sorbent porous structure. The model was then implemented and validated in the gPROMS ModelBuilder® software. In this work, data from fixed bed reactor experiments are used to validate both sub-models. Experimental data are used to justify the relationship between the loss of superficial area of CaO sorbents and the loss of carbonation conversion, which allows to extend the simulation to multiple reaction cycles.

## 2. Model Development

To simulate a complete CaL cycle, two different models were combined as sub-models: the OGM by Liu and Dennis (2012) for the carbonation reaction, and a proposed modified version (mRThPSD) of the rate equation theory for the pore size distribution (PSD) of calcined CaCO<sub>3</sub> (RThPSD) by Li et al. (2016) for the calcination reaction.

### 2.1. Carbonation – Overlapping Grain Model - OGM

The OGM grain model considers that each CaO particle is composed of solid and randomly distributed spherical grains with different sizes. The formation of CaCO<sub>3</sub> during carbonation reaction is assumed to happen at the grain surface, causing the grain's volume to expand concentrically, increasing its radius, and shrinking the radius of the CaO core.

The known two main reaction regimes of carbonation are considered: a kinetic controlled profile for small reaction times and a diffusional regime for longer reaction times. By modelling the particle as an aggregate of dynamic grains with shells of CaCO<sub>3</sub> and allowing for particle porosity, two mechanisms can control the rate of reaction. The

particle porosity allows the inclusion of the diffusion of CO<sub>2</sub> in the porous network, 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 front of reaction. In addition to the intrinsic reaction rate, these mechanisms contribute to more accurate carbonation simulations.

However, the OGM cannot estimate the maximum conversion for a given cycle and uses the deactivated fraction  $V_d$  as an input parameter, calculated as the difference between the theoretical maximum conversion and the experimentally observed conversion, that scales down the conversion estimated by the OGM to achieve the desired maximum conversion. The theoretical maximum conversion  $X_{Max}$  is a function of porosity of the initial CaO particle  $\epsilon_0$  and of the volumetric expansion coefficient between product and reactant  $\alpha$  and can be calculated using Eq. (1).

$$X_{Max} = \frac{\epsilon_0}{(1 - \epsilon_0)(\alpha - 1)} \tag{1}$$

The OGM allows for CaO particles with non-reacting impurities by considering their molar volume in the calculation of  $\alpha$ , as defined by Liu and Dennis (2012), thus this value varies between particles – e.g. 2.18 for pure CaO and 1.82 for dolomite. Due to this theoretical maximum conversion, there is an experimental limitation that should be accounted for when attempting to fit the OGM to data from carbonation experiments.

Figure 1 displays a plot of  $X_{Max}$ , with values larger than 1 computed as 1; and shows that  $X_{Max}$  is increasingly sensitive to the value of  $\epsilon_0$  as  $\alpha$  decreases. Generically, the porous characteristics of a sample of sorbent particles are not homogeneous, so it might occur that the porosity considered to be characteristic of a given sorbent sample of particles results in lower values of  $X_{Max}$  than the experimentally observed maximum conversion, which is of course impossible. As such, when fitting the model to the experimental results, and especially for the samples rich in CaO (e.g. commercial CaCO<sub>3</sub>), one should verify that this is not the case. If this condition is not verified, the variability of the sorbent sample porosity should be known and used to increase the value of  $\epsilon_0$  in the OGM to ensure that  $X_{Max}$  will at least equal the experimental maximum conversion, and only then should the parameter estimation be performed. With the maximum possible  $\epsilon_0$  being 1, the difference in sensitivity means samples less pure in CaO (e.g. dolomite) have more possible  $\epsilon_0$  values for which  $X_{Max} > 1$ , and thus it is less likely that the condition is not verified. Nonetheless, it can still happen, since ultimately it is the variability of sample's porosity that is more indicative of the likeliness of the condition not being verified – more likely for batches with high variability and less likely if otherwise.

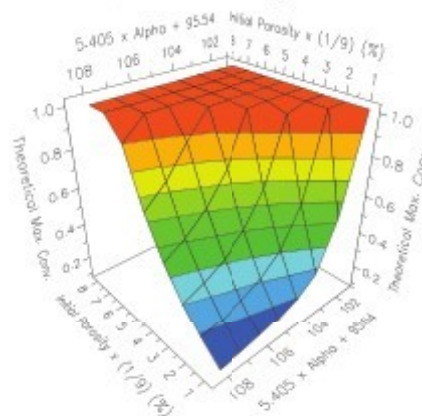


Figure 1 – Plot of the OGM's Theoretical Maximum Conversion (Eq. 1) for Initial Porosity between 0% and 60% and Alpha between 1.01 and 2.20.

## 2.2. Calcination – A rate equation theory for the PSD of calcined $\text{CaCO}_3$ - RThPSD

The RThPSD models the calcination reaction based on a shrinking core model, where a  $\text{CaCO}_3$  core leads to a shell of  $\text{CaO}$ . It also models the dynamics of the porous structure using a rate equation based on balances to the number of vacancies of various sizes. The original RThPSD considers that two phenomena can change the porous structure during the calcination reaction: the release of  $\text{CO}_2$  from the reaction, which creates vacancies by leaving the lattice; and the sintering process, which occurs naturally in  $\text{CaO}$  due to the high temperatures necessary for calcination.

The model, as presented by Li et al. (2016), has its shortcomings addressed by the modified version, mRThPSD, developed in this work, with the lack of initial conditions for the vacancy distribution being one those drawbacks. Without these, 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 is formed solely from the release of  $\text{CO}_2$  and from the sintering of those vacancies, which is not true, since the unreacted  $\text{CaCO}_3$  is already porous, as seen in the work of Dennis and Pacciani (2009). The final PSD is thus inextricably linked to the PSD of the unreacted  $\text{CaCO}_3$ . The mRThPSD model addresses this problem by deriving initial conditions from the PSD of the initial unreacted  $\text{CaCO}_3$ , through the assumption that the measured total pore volume for a given pore diameter is equal to the total volume of vacancies of that respective size, assuming these vacancies to be spherical. It is also assumed that these vacancies are homogeneously distributed throughout the particle. The initial conditions are calculated with Eq. (2), where  $N_{i,k,Initial}$  is the initial number of vacancies of size  $i$  in the  $k^{\text{th}}$  layer,  $V_{Pore,i}$  is the porous volume for pore diameter  $i$  of the unreacted  $\text{CaCO}_3$  in  $\text{m}^3\text{g}^{-1}$ ,  $Vol_{R_0}$  is the particle volume in  $\text{m}^3$  and  $k_{Layers}$  is the number of layers. The remaining variables and respective units are found in the original paper by Li et al. (2016).

$$N_{i,k,Initial} = \frac{V_{Pore,i} M_{CaO} Vol_{R_0}}{V_{CaO} v_i q^{i-1} k_{Layers}}, \forall \kappa \in [1, k_{Layers}] \quad (2)$$

Furthermore, in the original model, the area of the solid surface around the vacancies is calculated as the surface area of a sphere of the same diameter. However, sorbents for  $\text{CaL}$  are typically analyzed using  $\text{N}_2$  adsorption-desorption experiments together with the BJH model, where the cylindrical pores assumption, among others, leads to Eq. (3).

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 solid surface area generates values 1.5 larger than using Eq. (3). Since, as reported by Dennis and Pacciani (2009), the total pore surface area plays an important role in the carbonation reactivity of the sorbent, overestimating this property will skew future simulations towards unconservative conversion values. To address this, the mRThPSD assumes that the total surface area of pores of a given size is equal to the superficial area of a cylinder with the same total volume as the vacancies of the same size, calculated by Eq. (3) (SI units).

$$V_{Pore,i} = D_{Avg,i} S_i / 4 \quad (3)$$

Also, on the proposed mRThPSD the vacancy balance was modified to make the effects of  $\text{CaCO}_3$  decomposition and  $\text{CaO}$  sintering simultaneous. Also, an error was corrected in the vacancy balance where the total volume of vacancies would decrease, which does not occur during calcination, as stated in the work by Li et al. (2016), as no pore straightening mechanism is present. Figure 2 highlights this error by showing the evolution of the total pore volume along the time during simulation with the original balance versus with the modified balance. The decrease in pore volume in the original balance is very apparent in Figure 2, caused by the artificial volume consumption brought on by this error being larger than the vacancy generation. As for the modified balance, it is possible to see that the volume created is conserved, as expected.

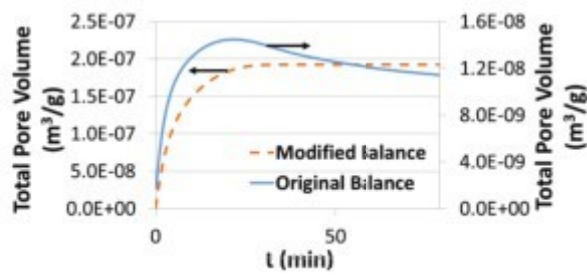


Figure 2 – Total Pore Volume along time using the Original and the Modified Vacancy Balance in the RThPSD model;

### 3. Results

Experimental data from fixed bed reactor experiments were used to validate both models. The OGM was validated for three different sorbents: commercial  $\text{CaCO}_3$ , dolomite, and waste marble powder, a residue from the Portuguese marble industry, shown to have economic potential as a CaL sorbent (Pinheiro et al., 2016). As for the mRThPSD, it is currently only validated for dolomite due to the extensive experimental work required, and its validation with other sorbents is underway. The OGM was able to replicate both reaction regimes for all sorbents with an excellent accuracy, as shown on Figure 3 and by an average error of approximately 2%, for all sorbents. The reaction regimes are highlighted for the dolomite series as line segments i and ii (Figure 3). As for the validation of the mRThPSD, in terms of the estimation of the post-calcination particle's total pore volume, Figure 4 shows a quite satisfactory fitting, considering the complexity of the system. Despite observing that part of the volume allocated to the peak of the mRThPSD post-calcination curve should be located in higher pore diameters, there is an excellent agreement between the estimated and the experimental total pore volume, with a deviation of approximately 3%. As for the calcination conversion profile the proposed

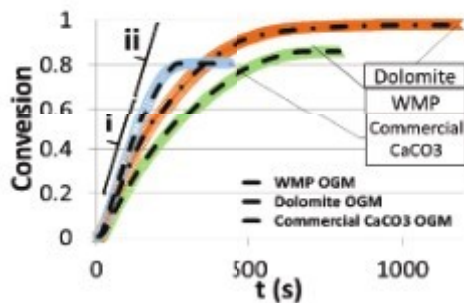


Figure 3 – Validation of the OGM for different sorbents (700 °C, 0.15 bar  $\text{CO}_2$ ). Reaction domains for Dolomite: i – Kinetic Regime, ii – Diffusional Regime;

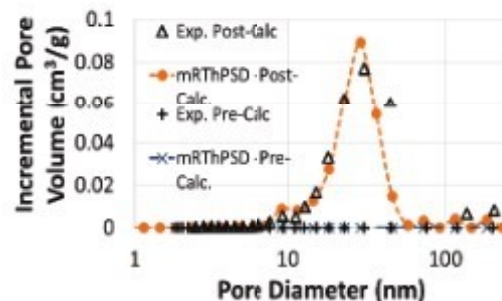


Figure 4 – Validation of the mRThPSD for Dolomite (800 °C, 0%  $\text{CO}_2$ );

mRThPSD can estimate it precisely, with an average deviation of approximately 1.2% to the experimental results. The fact that the solid's porous structure influences the reaction rate, highlights the necessity of an adequate fitting to the evolution of the particle's PSD, as seen in Figure 4. However, the inclusion of Eq. (3) limits the effect of an imperfect fit to the superficial area, whereas the overestimation of this

property in the original model would result in lower diffusivity values and thus lower reactions rates, hindering the fitting to the conversion profile. As for the cyclic structure of the model, it was implemented using the relationship between the loss of superficial area and sorbent deactivation, shown on Figure 5. This was used to redefine the OGM's deactivated fraction  $V_d$ , thus connecting the sub-models. The mRThPSD estimates the total loss of area during calcination, which determines the extent of the following carbonation. Figure 5 shows the importance of using the mRThPSD to model these mechanisms to estimate sorbent deactivation in the case of incomplete reactions, different temperatures and  $\text{CO}_2$  partial pressures.

#### 4. Conclusions

A new model that combines carbonation and calcination was implemented in gPROMS ModelBuilder<sup>®</sup>. Both sub-models were successfully validated using data from fixed bed reactor experiments, for three different sorbents, commercial  $\text{CaCO}_3$ , dolomite, and waste marble powder, a Portuguese marble industry residue, recently shown to have economic potential as an industrial sorbent for CaL. The predicted values have errors below 3% for both sub-models, when compared to experimental results. Only dolomite was used for the validation of mRThPSD and further experimental work with other sorbents is underway. The proposed model contains a cyclic structure accounting for sorbent deactivation, based on the relationship between loss of superficial area of CaO sorbents and loss of reactivity. While only one cycle was simulated in this work, experimental work is underway to validate the cyclic structure for more reaction cycles.

#### References

- J. S. Dennis, R. Pacciani, 2009, The rate and extent of uptake of  $\text{CO}_2$  by a synthetic, CaO-containing sorbent. *Chemical Engineering Science*, 64, 9, 2147–2157.
- Z. S. Li, P. T. Liang, N. S. Cai, 2016, A rate equation theory for the pore size distribution of calcined  $\text{CaCO}_3$  in calcium looping, *Faraday Discussions*, 192, 197–216.
- W. Liu, J. S. Dennis, S. Sultan, S. A. T. Redfern, S.A. Scott, 2012, An investigation of the kinetics of  $\text{CO}_2$  uptake by a synthetic calcium based sorbent, *Chemical Engineering Science*, 69, 1, 644–658.
- C. I. C. Pinheiro, A. Fernandes, C. Freitas, E. T. Santos, M. F. Ribeiro, 2016, Waste marble powders as promising inexpensive natural CaO-based sorbents for post-combustion  $\text{CO}_2$  capture, *Industrial & Engineering Chemistry Research*, 55, 29, 7860–7872.
- Z. Zhou, P. Xu, M. Xie, Z. Cheng, W. Yuan, 2013, Modeling of the carbonation kinetics of a synthetic CaO-based sorbent, *Chemical Engineering Science*, 95, 283–290.

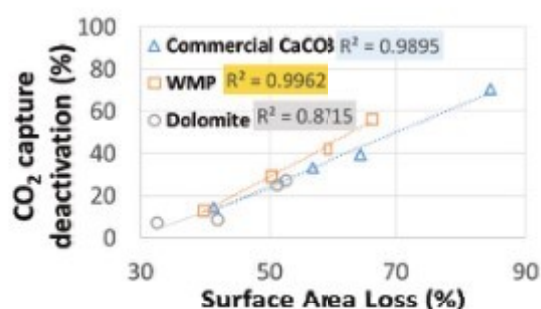


Figure 5 – Sorbent Deactivation (%) Vs. Surface Area Loss (%) for cycles 2, 5, 10 and 20 (from left to right);