

SEM analysis application to study CO₂ capture by means of dolomite

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1. Introduction

Pure hydrogen from renewable sources can be obtained by a steam gasification process where syn gas is depleted of its carbon-containing compounds by means of CO₂ capture with calcined dolomite.

Steam gasification processes are able to convert the chemical energy of biomass into a hydrogen-rich syn gas containing up to about 50% by volume of hydrogen on dry basis [1]. On the whole, the biomass gasification reactions are globally endothermic; when part of the fuel is burnt by oxygen, in the same reactor chamber, to allow for an auto-thermal process, the hydrogen molar fraction reduces to about 35% on dry basis [2].

Biomass gasification addressed to maximize the yield of a clean (substantially free of heavy organic compounds, collectively defined as tar) gaseous product needs to be performed at relatively high temperature (800-900°C [3]): a thermally efficient process would imply the use of perm-selective membranes made of palladium or its alloys, and operation under pressure would have some technical and economic drawbacks. For such reasons, we are studying the practical feasibility of the syn gas treatment with calcined dolomite, to separate carbon dioxide, and regeneration of exhausted dolomite by calcination.

Magnesium oxide, also contained in calcined dolomite, does not contribute to carbon dioxide sequestration, because magnesium carbonate decomposes at much lower temperature than calcium carbonate, however inert MgO contributes to stabilize the structure of the solid sorbent in a multi-cycle carbonation-calcination process [4].

Thermodynamics shows that, in the temperature range 600-650°C, a dry gas containing up to 98% by volume of H₂ is obtainable [5]. In order to keep uniform temperature conditions in presence of a considerable extent of both, exothermic and endothermic reactions, a fluidized bed reactor is proposed, operating adiabatically and isothermally at atmospheric pressure. In these conditions, according to model estimations, CO₂ uptake by calcium oxide contained in the dolomite particles is a relatively fast reaction process provided that particle size is sufficiently small. The solid sorbent needs to be regenerated cyclically, by addition of heat: this could be done in a way (for example: coke combustion with oxygen and steam) that allows recovering of a pure CO₂ stream, to be stored or utilized to different purposes.

Depleting of the syn gas carbon-containing compounds by means of CO₂ capture with calcined dolomite is the scope of this investigation. Experimental studies of the optimal operating temperatures and characterization of the heat treated dolomite have been

carried out, in order to understand the dolomite behavior as CO₂ sorbent and to validate a proposed modeling approach.

Model predictions indicate that, with grain sizes of the order of those effectively measured in practice, calcium oxide is converted to calcium carbonate over time intervals of the order of a few minutes or less, which are compatible with a bubbling fluidized bed reactor design. Experimental data obtained in our laboratory and available in the recent literature will be presented and compared with calculated values.

2. Experimental studies

The thermal behavior (weight losses, exo- and endo-thermic reaction temperatures, gas evolution) of dolomite as CO₂ sorbent and its regeneration has been investigated by means of a Linseis TG-DTA coupled with FT-IR spectrometer.

Original and heat-treated dolomite has been characterized by XRF and SEM with backscattered electrons, BSE, in order to measure the composition and the morphology and the compositional profiles of polished samples of dolomite particles. SEM analysis with backscattering electrons, BSE, has been used in the characterization of the original and heat treated dolomite particles. Powder samples have been incorporated in an epoxy resin and subjected to a lapping process in order to obtain the particle section. The surface of the so incorporated samples has been covered with a golden film to prevent conductivity problems.

The experimental study has been performed with Pilkington dolomite (kindly provided by Pilkington Ltd), with an average particle diameter of 165µm and a particle density of 2665 kg/m³.

The powder weight percent composition has been obtained by means of X-Ray Fluorescence spectrometer detecting all atomic mass $Z \geq 12$ chemical elements.

Z	Symbol	Concentration	Abs.Error
		%	%
12	Mg	12,58	0,045
20	Ca	23,98	0,030
	other	< 0,35	

Table 1 Composition of Pilkington dolomite (Loss of ignition 63%)

The thermal analyses have been carried out at a heating rate of 10°C/min in different atmospheres with gas flow rate of 2l/min.

In Figure 1 the DTA and TG curves of dolomite heat treated in different atmospheres until 1000°C, with an heating rate of 10°/min, have been reported. The DTA curves highlight two endothermic peaks, corresponding to the heat absorbed by calcination of magnesium and calcium carbonate, with maxima at the temperatures Tp1 and Tp2, respectively. In correspondence of DTA peaks, the TG curve shows a weight loss of about 50%, close to the theoretical one for the complete decomposition of carbonates, calculated from the elemental analysis. In stagnant air the weight losses are slightly lower than in gas flow. No sintering processes take place after calcination, up to 1000°C.

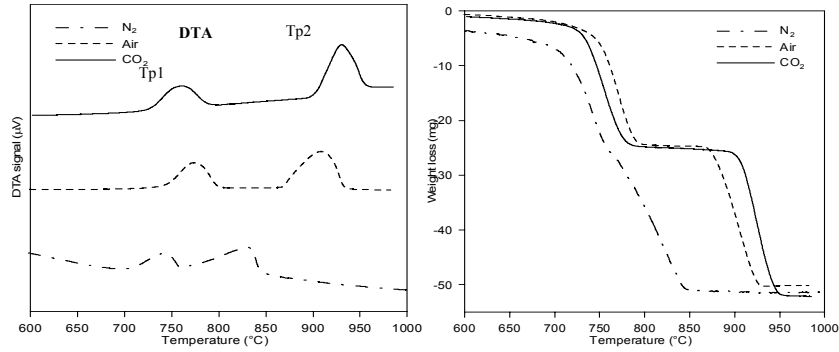


Fig. 1: DTA and TG of calcination steps of 165µm dolomite particles ($\Delta T= 10^{\circ}C/min$)

In table 2 the T_p values are reported for each atmosphere. It can be observed that T_{p2} , corresponding to $CaCO_3$ calcination, increases in CO_2 flow and decreases in N_2 flow, as expected, with respect to stagnant air; T_{p1} , corresponding to $MgCO_3$ calcination, decreases, whichever the flow, with respect to stagnant air.

	T_{p1}	T_{p2}
	($^{\circ}C$)	
N_2	741	830
Air	773	909
CO_2	760	930

Table 2: DTA peak temperatures: T_{p1} $MgCO_3$ and T_{p2} $CaCO_3$ decarbonation

We conclude that, at least with a fresh sample, magnesium and calcium carbonate are completely decomposed at relatively low temperature, and over time intervals of the order of a few minutes, which are compatible with a bubbling fluidized bed reactor design.

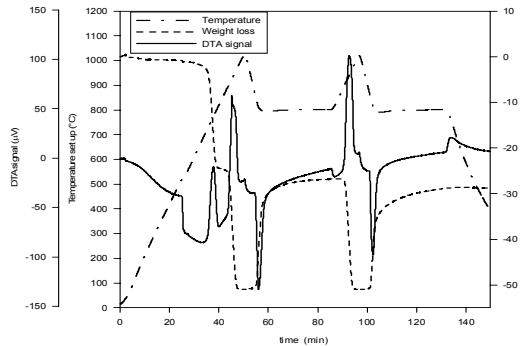


Fig. 2: Two calcination-carbonation cycles with step temperature at $800^{\circ}C$

A DTA at 10°C/min heating rate until 1000°C and cooling in CO₂ flow has been carried out in order to investigate the carbonation of the calcined dolomite, i.e. its behavior as CO₂ adsorbent. The CaO carbonation peak has been individuated at 811°C.

In Figure 2, the TG-DTA curves, simulating two cycles of CO₂ adsorption and dolomite regeneration, have been reported. The dolomite has been heat treated at 10°C/min until 1000°C and cooled in CO₂ flow until 800°C with a 30 minutes dwell time twice. Three major peaks are obtained in the DTA signal: the endothermic peaks at 765°C and at 940°C, refer to the heat absorbed by magnesium carbonate and calcium carbonate, respectively. The exothermic peak at around 790°C corresponds to CaO carbonation process.

It is observed that no sintering processes take place also in CO₂ flow as confirmed by SEM micrographs. On the pictures (fig. 3), after 1h of heat treatment of sample at 850 °C, we can observe small pores in calcined dolomite and sintering bridges in calcined limestone as indicated in the circle.

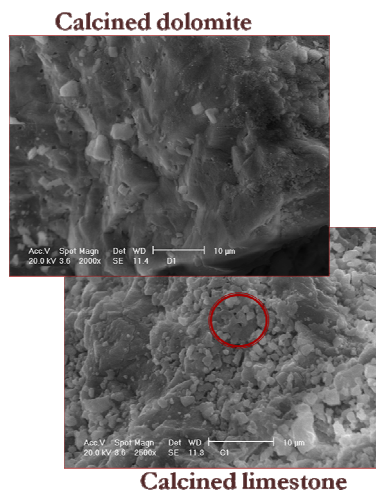


Fig. 3: SEM analysis of calcined dolomite and limestone

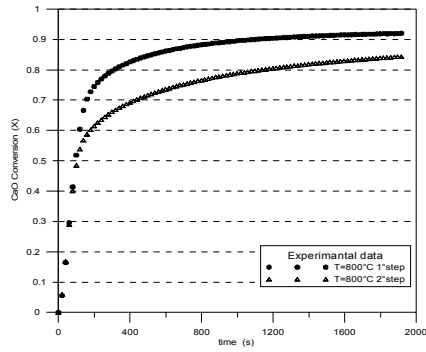


Fig. 4: CaO conversion vs. time

In Figure 4, we show in details TG experimental data for the carbonation steps: in the first cycle at 800°C we obtained more than 90% CaO conversion in about 20 minutes, while the conversion doesn't reach 85% once the dolomite has been regenerated.

Original and post-cycle dolomite powders have been observed in Figures 5-8.

In the original dolomite polished sample (Fig. 5-6) at increasing magnification ratio, it's possible to observe a quite uniform composition, even if there are some impurities (metallic elements), and a structural uniformity; this doesn't occur at boundary layers of the particles, where some fractures are caused by mechanical stresses; micrographs highlight a crystalline structure of the virgin sorbent.

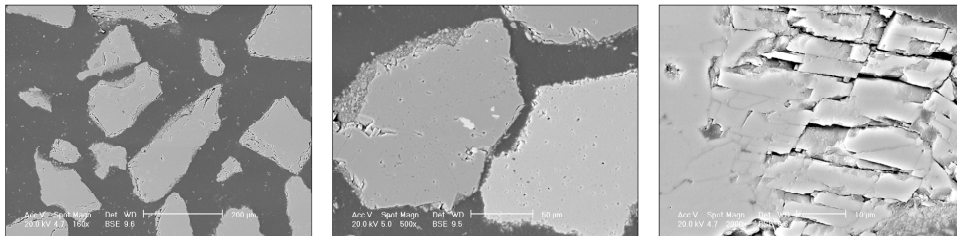


Fig. 5: Original particles of Pilkington dolomite

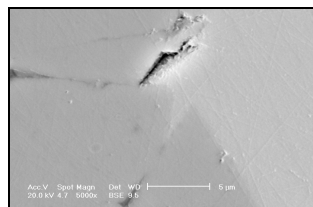


Fig. 6: Particle details of original dolomite

As displayed in Figure 6, lines are caused by the lapping process and crystallization

levels are very visible.

In Figure 7, polished sample treated in a fixed-bed reactor (2 calcination-recarbonation cycles) in CO₂ flow, are shown: it is possible to observe the presence of fine particles, diameter <20µm, absent in the original dolomite, highlighting that dolomite, when subjected to repeated cycles of calcinations/re-carbonation, becomes friable. The loss of mechanical resistance and the physical degradation of dolomite could be an explanation of why the degree of re-carbonation decreases with the number of heat treatment cycles in DTA. Despite the significant fragmentation - due to the mechanical and thermal stresses - a grain structure in the whole mass of the particle has been observed, and the experimental value of CaO grain size can be estimated of the order 1-2 µm.

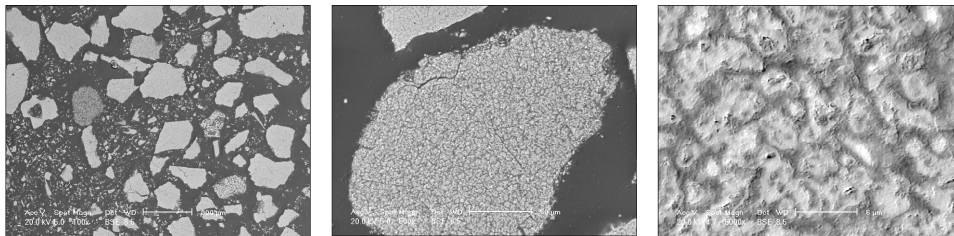


Fig. 7: on the left, particles of Pilkington dolomite after two cycles at 800°C (100 X); in the middle, a single particle of Pilkington dolomite after two cycles at 800°C (500 X); on the right, a detail of previous particle (5000X)

In the SEM - BSE pictures, an external carbonate shell (light zones) surrounding unreacted calcium oxide (dark zones) can be individuated at grain scale.

These results allow to define a particle reaction model for dolomite re-carbonation, as it is done in the next chapter; it is worth noticing that, at the grain scale, once the overall grain surface is converted to CaCO₃, the only possibility for CO₂ to reach the unreacted CaO core is by diffusing through the shell of the reaction product, a much slower mechanism than percolation through particle pores. These findings could justify why in the TG tests the degree of conversion of CaO never reaches 100% over limited time ranges.

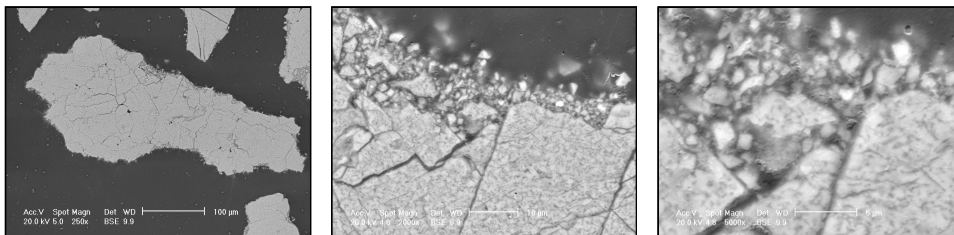


Fig. 8: Polished sample exposed to two calcination-recarbonation cycles in a fluidized-bed reactor.

In Figure 8, a polished sample exposed to two calcination-recarbonation cycles in a fluidized-bed reactor is shown. A grain structure is visible also in this case, however the final conversion of CaO into CaCO₃ appears greater than that obtained in the TG test (Fig. 7), as it is also confirmed by quantitative measurements [6]: this could be ascribable to the optimum reaction conditions chosen in the fluidized bed tests.

3. Modeling approach

As a starting point, a spherical grain model is assumed to describe the re-carbonation process of dolomite particles: the specific active surface, σ_{CaO} , is proportional to the number of calcium oxide/carbonate grains per unit particle volume, and to the surface of each grain corresponding to the volume occupied by the un-reacted calcium oxide, which in turn is assumed to keep a spherical shape.

The fluidized bed reactor is characterized by a small size of its granular solid inventory ($d_p \leq 200 \mu m$), and a similar consideration applies to the TG tests: as a result, intra-particle and boundary layer diffusion can be neglected as a first approximation, and reaction assumed to occur uniformly throughout the particle. A linear dependency of the kinetic expression on CO₂ gas concentration is also assumed, because it is consistent with previous literature studies [7] and our experimental findings. It may be concluded that the reaction rate could be well correlated by:

$$N_{0Ca} \frac{dX}{dt} = k \sigma_{CaO} (C_{CO_2} - C_{CO_2,eq}) \quad (1)$$

where the amount of calcium g-atoms per unit particle volume, N_{0Ca} , is obtained from the knowledge of the CaCO₃ mass fraction, f , in fresh dolomite, and the particle density ($N_{0Ca} = f \rho_D / M_{CaCO_3}$).

The equilibrium pressure of carbon dioxide (in atm) is known as a function of temperature [8]:

$$P_{CO_2,eq} = 4.137 \cdot 10^7 e\left(-\frac{20474}{T}\right); \quad C_{CO_2,eq} = \frac{P_{CO_2,eq}}{RT}$$

According to the above assumptions, when the initial (after calcination) CaO grain diameter, δ_{CaO} , is chosen, and its maximum reachable conversion, X_f , fixed, the following equations allow to express σ_{CaO} :

$$\begin{aligned} \sigma_{CaO} &= \frac{N_{0CaO} V_{CaO}}{\pi/6 \delta_{CaO}^3} \times \pi \delta_{CaO}^2 (X_f - X)^{2/3} \\ &= N_{0CaO} V_{CaO} \frac{6}{\delta_{CaO}} (X_f - X)^{2/3} \end{aligned} \quad (2)$$

The above relation establishes the dependency of the specific active surface on the dolomite physical and chemical properties, the particle texture (the average grain size, δ_{CaO}), and the calcium oxide conversion. The grain size in our model is chosen to be included in the interval 1-2 μm , which agrees with measurements made on SEM micrographs; with this assumption, the initial surface area (after calcination), σ_{0CaO} , is

found close to $2 \text{ m}^2/\text{cm}^3$.

An average value for the intrinsic rate constant, $k^2=k/N_{0\text{Ca}}$, has been determined experimentally and reported in the literature; it is equal to $0.0595 \text{ cm}^4/\text{mol}\cdot\text{s}$, with zero activation energy in the temperature range 823-998 K [9]. As a result, the integration of equation (1) gives the conversion profiles as a function of time, as shown in Figure 9, where the model predictions are compared with experimental data of $250 \text{ }\mu\text{m}$ dolomite particles carbonation at 550°C [10], and in presence of different partial pressure of carbon dioxide; moreover we observe that these data don't show a sigmoidal shape of the conversion curves. A very good agreement is obtained for all experiments when the CaO grain size is assumed equal to 1660 nm . However, the initial carbonation rate is not well simulated for each CO_2 pressure.

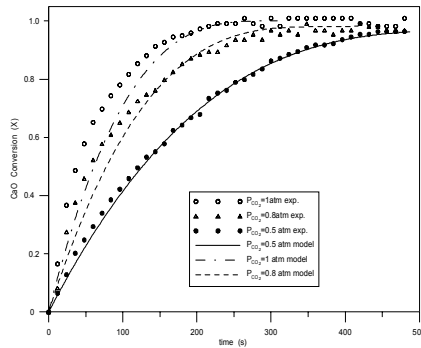


Fig. 9: Experimental data [9] and spherical grain kinetic model ($\delta_{\text{CaO}}=1660\text{nm}$)

At the beginning, experimental conversion degree is greater than the calculated one because in the model the pore surface has been neglected. As the conversion goes on, the pore surface decreases and the model prediction improves.

When our experimental data are simulated, we have to introduce corresponding values for physical and chemical properties of Pilkington dolomite. For example, $f=0.599$ and the correct final conversion has to be taken from results in Figure 4. Calculated results are shown in Figure 10.

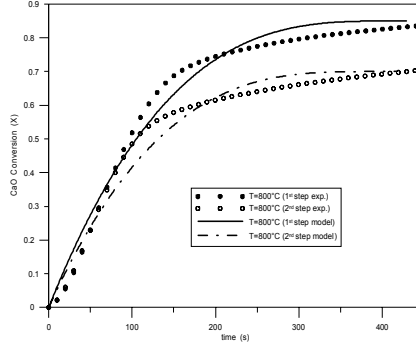


Fig. 10: Experimental data and spherical grain kinetic model ($\delta_{CaO} = 1660\text{nm}$ at 800°C)

At the beginning the calculated data are greater than the experimental ones as the diffusive term has been neglected, in a second time range, $90 \div 180\text{s}$, the calculated data are lower than the experimental ones because of pore surface neglecting. When the conversion degree overcomes 0.7, for the first cycle, and 0.6, for the second one, the experimental data are lower than those the model predicts as the products of reaction obstructs the pores and covers the surface.

Because of the increasing formation of calcium carbonate at the grain surface, diffusion through the product layer of calcium carbonate could become important.

This phenomenon could explain calcium oxide conversion reaching almost a plateau at a value, $X=X_f$, somewhat lower than one. The abrupt change in the slope of $X(t)$ could be related to product layer diffusivity, D_{PL} , becoming the controlling step of the whole reaction-diffusion process.

The effect of the product layer diffusion resistance on the reaction rate can be computed by means of the application of the shrinking core model, which hypothesizes that reaction occurs in the outer coat of the particle and a thin reactor front is formed, moving towards the particle center and leaving backwards a product layer as the reaction progresses [11]. This model has been applied at a single calcium containing grain, taking into account that a porous structure consisting in a grain matrix highlighted in the carbonated dolomite SEM pictures (Figure 7).

By imposing that the rate of diffusion through the product layer should be equal to the reaction rate at the core surface, a global kinetic relationship (SRD Model) can be easily derived:

$$\frac{dX}{dt} = \frac{\sigma_{0,CaO} k_{BP} (X_f - X)^{2/3} (C_A - C_{Ae})}{1 + \frac{N_{Ca} k_{BP}}{2D_{PL}} \delta_{CaO} \sqrt[3]{1-X} \left(1 - 3 \sqrt[3]{\frac{1-X}{1-X+X \cdot Z}} \right)} \quad (3)$$

where Z is the calcium carbonate/oxide molar volume ratio, >1 .

The product layer mass transfer resistance can be:

- either considered since the beginning of the CO_2 absorption process,

- or a transition should be imposed between “straight reaction” at the grain surface, as illustrated in the section above, and “product layer diffusion followed by reaction (SRD model)”[12].

In order to integrate the previous equation, together with the initial and boundary conditions, to obtain CaO conversion as a function of time, we have used a standard code (MATHCAD^v)

This transition (X_{trans}) should take place at a later stage of the dolomite carbonation process, fixed in agreement with the experimental evidence. Experimental data (points) and SRD model predictions (continuous lines) at 800 °C ($D_{PL} = 1 \times 10^{-8} \text{ cm}^2/\text{s}$; $\delta_{CaO} = 1150 \text{ nm}$; transition to SRD mechanism: $X_{trans}/X_f = 0.83$) are shown in Figures 11 and 12.

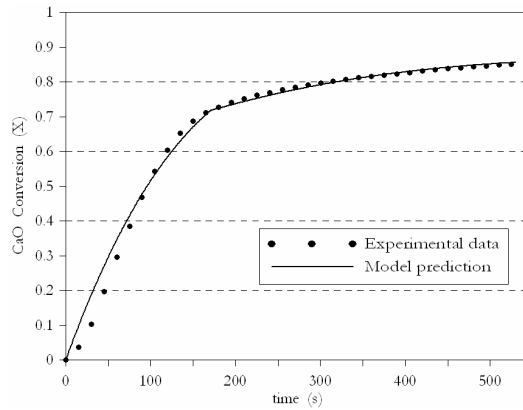


Fig. 11: First carbonation cycle of calcined dolomite at 800°C (experimental data and model prediction)

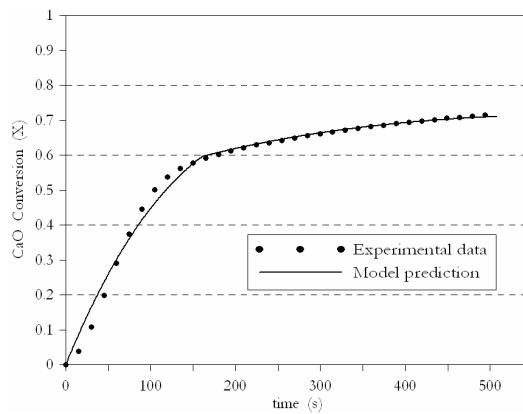


Fig. 12: Second carbonation cycle of calcined dolomite at 800 °C (experimental data and model prediction)

Conclusions

The experimental studies show the ability of calcined dolomite results in being a good sorbent of CO₂ with CaO re-carbonating at a temperature of about 800°C. According to DTA, it's possible to calcine dolomite practically at this same temperature with adequate gas flow. The degree of conversion of CaO in CaCO₃ decreases with the number of calcination/re-carbonation cycles as the dolomite degrades.

The data obtained by TG/DTA tests show that with small particle sizes calcium oxide is converted to calcium carbonate over time intervals of the order of a few minutes, compatible with a bubbling fluidized bed reactor design and the SEM analysis of virgin and calcined dolomite samples have shown the presence of a particle grain structure, with average size of 1 – 2 μm.

The spherical grain model applied, in order to study the separation process of carbon dioxide from syn gas, show that a simple analytical solution is possible.

Despite the absence of diffusivity term and the neglecting of the pore surface, the simulated results are in reasonable agreement with experimental data and the overall carbonation time is predicted reliably.

The results of this work show good agreement between the SRD model predictions and experimental data obtained either by SEM micrographs of dolomite particles at different stages of the calcination/carbonation cycles, and by TG curves of CaO conversion as a function of time. This model is able to fit accurately the experimental kinetic data with the application of a double mechanism: chemical reaction on the grain surface, followed by product layer diffusion and chemical reaction at the later stage of the sorption process.

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