

LIMESTONE AND DOLOMITE AS THERMOCHEMICAL ENERGY STORAGE MATERIALS: REACTION KINETICS AND DEACTIVATION MODELING

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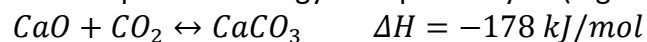
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ABSTRACT

A comparative study for dolomite and limestone was conducted regarding the Ca-L reaction kinetics and deactivation, both experimentally in a fixed-bed reactor apparatus and theoretically. A RPM for each reaction was used based on the initial material's properties to predict the surface area evolution during the reaction, while the apparent reaction rate r was a function of reaction temperature and CO₂ partial pressure. Carbonation reaction was completed in less than 10 seconds for both tested materials under P_{CO2}=1.25 atm and T=850°C. Dolomite and limestone exhibited similar reaction rates during carbonation stage and the reaction was adequately modelled for both materials calculating the pre-exponential factor $k_0=6,9E-06$ m⁴/(kmol s) and finding a first order dependence on the P_{CO2}. The same procedure for calcination reaction showed that dolomite decomposed faster than limestone owing to its higher surface area. Dolomite was fully calcined in 1.5 atm of pure CO₂ in almost 60 seconds. An exponential decay of the rate with respect to P_{CO2} was observed, while the pre-exponential factor was found equal to 5.5 m/s. The deactivation study showed that dolomite achieved higher maximum conversions through the cycles and exhibited half the deactivation of limestone.

INTRODUCTION

Energy storage systems are of great importance for the on-demand use of seasonal renewable sources, such as solar energy. Calcium looping (CaL) has been proposed to be used as thermochemical energy storage (TCES) system in concentrated solar power (CSP) plants [1]. Accordingly, the solar energy can drive the endothermic reaction in a calciner reactor, while the reverse carbonation reaction will produce energy via a power cycle (e.g. Rankine cycle).



This is a promising alternative to the molten salts technology which is characterized by short time storage as well as low operating temperatures. On the other hand, carbonation reaction is highly exothermic and can take place at temperatures ~850°C, increasing the power cycle efficiency. Other advantages are the non-toxicity and availability of raw materials, as well as their capability to be stored for long time periods at ambient conditions. Two candidate materials are limestone and dolomite, which both are abundant and low cost minerals. Herein, these two materials are comparatively studied with regards to their reaction rates and conversion through the CaL cycles.

REACTIONS KINETICS AND DEACTIVATION MODELING

The kinetic modelling of the CaL reactions was achieved by using two Random Pore Models (RPMs), one for each reaction. The overall conversion rate (da/dt) is assumed to be proportional to the available solid surface area, which changes during the reaction in a way that RPM predicts. The fitting parameter of the RPM is the apparent reaction rate r which in turn is a function of reaction temperature and CO₂ partial pressure. The main assumptions made for the kinetic modelling are i) the particles are isothermal, ii) internal and external mass and heat transfer resistances are relatively small compared to that of the reaction and iii) no pre-mature pore mouth blocking is caused.

1. Calcination & carbonation reactions

The model used for the description of calcination reaction is adopted by Gavalas ^[2], who proposed an expression of the fractional conversion versus time, which takes into consideration the intersections' probability of randomly distributed pores while the reaction proceeds. The time evolution of the fractional conversion (α) according to RPM is given by:

$$\alpha(t) = 1 - \exp(-S_0 r t - \pi L_0 (r t)^2) \quad (1)$$

Where S_0 and L_0 are the surface area (m^2/m^3) and mean pore length area (m/m^3) of the initial material respectively, r –the fitting parameter- is the apparent reaction rate (m/s) and t is time (s). The overall conversion rate (da/dt) here is equal to the reaction front motion rate in velocity units. Eq. (1) shows the dependence of the overall conversion rate on the initial surface area and mean pore length of the material before the calcination begins. Two different materials were measured and compared with respect to their calcination reaction rate, namely the limestone (approximately pure CaCO_3) and the CaCO_3 derived by dolomite, which actually is CaCO_3/MgO , as the MgCO_3 has been already decomposed at such high temperatures. *Table 1* summarizes the textural properties of these two materials used in the calcination experiments.

Similarly to the calcination reaction, the RPM model used ^[3] for describing the carbonation reaction considers the pore structure as a network of randomly interconnected pores, and calculates the fractional conversion versus time using structural properties of the initial material:

$$\alpha(t) = 1 - \exp\left(\frac{1 - \left(\frac{\tau \Psi + 1}{2}\right)^2}{\Psi}\right) \quad (2)$$

Where τ is the dimensionless time given by:

$$\tau = \frac{r S_0 t}{1 - \varepsilon} \quad (3)$$

and Ψ is a structural parameter of the initial material containing S_0 , L_0 and ε :

$$\Psi = \frac{4\pi L_0 (1 - \varepsilon)}{S_0^2} \quad (4)$$

The materials that were subjected to carbonation were CaO derived from limestone (pure CaO) and dolomite (CaO 69%wt. with MgO) after calcination. The structural properties of these two pre-carbonation materials are shown in *Table 1*.

Table 1. Initial values of limestone and dolomite properties used in the RPMs.

Property	Limestone		Dolomite	
	Calcination	Carbonation	Calcination	Carbonation
BET surface area (m^2/g)	1.19	16.97	7.47	21.3
Mean particle diameter, d_p (m)	0.00006	0.00006	0.00006	0.00006
Mean Pore Length, L_0 (m/m^3)	2.06E+13	2.79E+14	9.06E+13	3.15E+14
Pore Volume, V_0 (m^3/g)	1.34E-08	1.73E-07	1.06E-07	2.02E-07
Mean pore radius, r_0 (m)	2.33E-08	2.04E-08	2.86E-08	2.07E-08
Porosity, ε_0	0.035	0.366	0.232	0.424
Ψ	-	1.72	-	1.35

The reaction rate r derived from the fitting of RPMs to the experimental data is a function of temperature and CO_2 partial pressure as follows:

$$r(T, P_{\text{CO}_2}) = k_0 \exp\left(-\frac{E_a}{RT}\right) f\left(\frac{P_{\text{CO}_2}}{P_e}\right) \quad (5)$$

where P_e (atm) is the equilibrium CO_2 partial pressure at the reaction temperature and is calculated by ^[4]:

$$P_e = 4.083E07 e^{-\frac{20474}{T}} \quad (6)$$

Thus, the reaction rate r contains an Arrhenius term with the pre-exponential factor k_0 and the activation energy E_a , and a function of P_{CO_2} and P_e . There is a large amount of scientific work focusing on the CaL reactions mechanism determination but without agreement yet.

2. Deactivation modeling

In order to model the deactivation rate in CaO conversion during multiple cycles, the following equation was used ^[4]:

$$\frac{X_N}{X_1} = \frac{X_r}{X_1} + \left(\frac{1}{k(N-1) + \left(1 - \frac{X_r}{X_1}\right)^{-1}} \right) \quad (7)$$

where, X_N is the conversion in cycle N , X_r the residual conversion, X_1 the conversion in the first cycle and k the deactivation rate constant. Two fitting parameters can be derived from the above equation: the deactivation constant and the residual conversion.

EXPERIMENTAL

The carbonation/calcination experiments were carried out in a continuous flow unit, consisting of the gas feed inlet section, the reactor and the product analysis section. The incoming gases are controlled by mass flow controllers and are pre-mixed before entering the reactor. A fixed bed quartz reactor equipped with a coaxial thermocouple for temperature monitoring, was used for the testing. The hot gases exiting the reactor are cooled down to room temperature and continuously analysed by a mass spectrometer (MS). The materials used were a limestone (Granicarb 0.1/0.8) and a dolomite (Mikrodol 1KN), both from OMYA S.A. company. The sorbent materials were sieved in the range of $45 < d_p < 75 \mu\text{m}$ and each time 100 mg were mixed with 1.5 g of quartz with particle size of $100 < d_p < 180 \mu\text{m}$ and loaded in the reactor. The total gas flows during calcination and carbonation were in the range of 500-600 ml/min (GSHV=22500-27000h⁻¹).

RESULTS AND DISCUSSION

1. Carbonation kinetics

The two CaO-based materials (derived from dolomite and limestone) were subjected to carbonation at $T=850^\circ\text{C}$ and flow of pure CO₂ with $P_{\text{CO}_2}=1.25 \text{ atm}$. Dolomite achieved higher and almost complete conversion compared to limestone which attained just over 60% during the first cycle (*Figure 1a*). This difference is attributed to the lower CaO content (69% wt.) distributed to the higher surface area of CaO/MgO (21.3 m²/g) compared to the lime's (16.97 m²/g). The two materials exhibited similar reaction rates (*Figure 1b*), due to the fact that during the surface reaction controlled regime both materials consume the available CaO at the same time period.

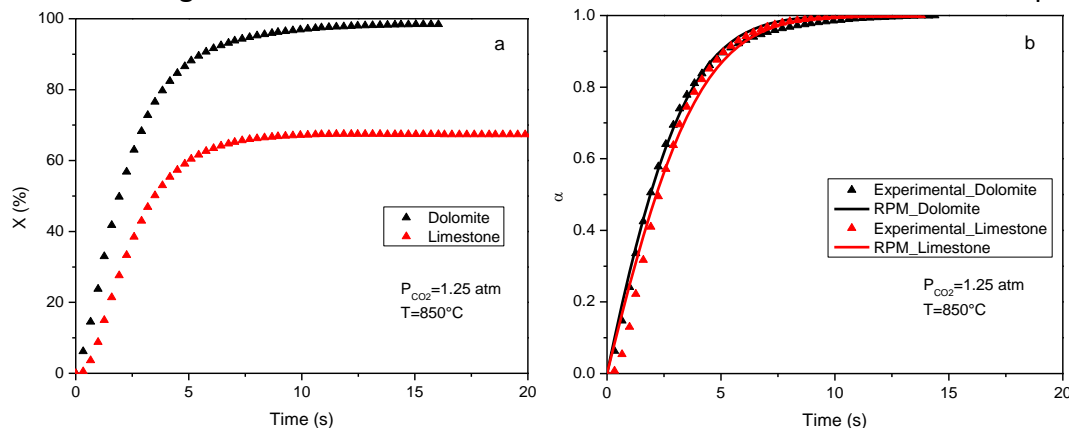


Figure 1. Conversion vs time (a) and fractional conversion vs time (experimental data and RPM) (b) for carbonation reaction of dolomite and limestone derived CaO under $P_{\text{CO}_2}=1.25 \text{ atm}$ and $T=850^\circ\text{C}$.

In order to determine the reaction order with respect to P_{CO_2} , carbonation of dolomite was carried out under different CO₂ partial pressures (1.25, 1.0 and 0.8 atm) (Figure 2a). The decrease of P_{CO_2} causes a reduction of the reaction rate which approaches the first order. The r vs $(P_{\text{CO}_2}-P_e)$ line deviates from passing through the axis origin maybe due to the non-isothermal conditions inside the particles (Figure 2b).

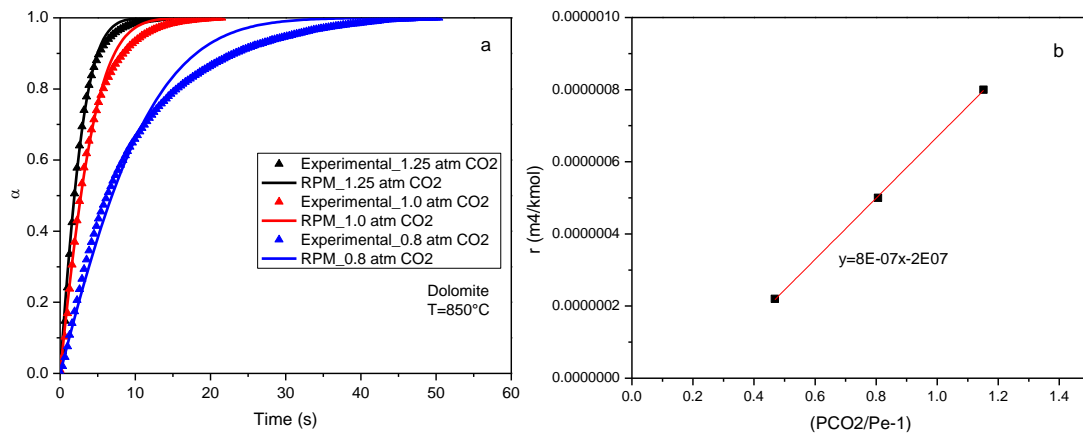


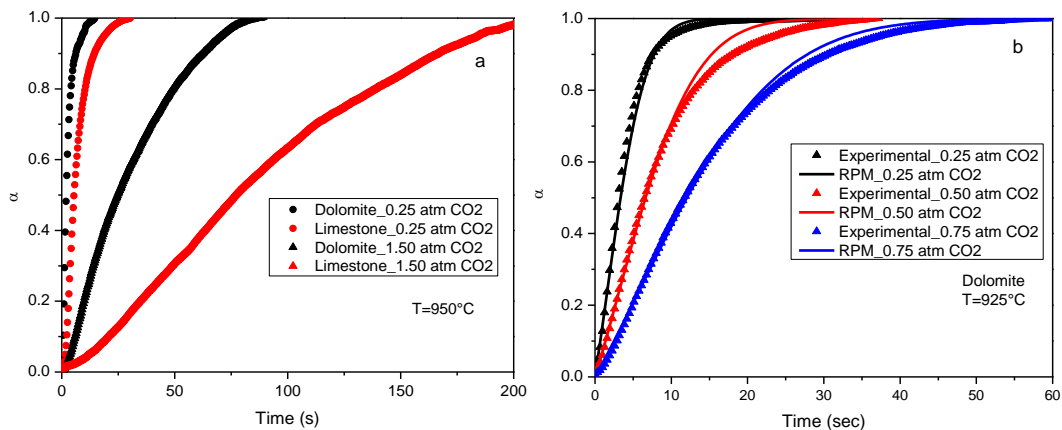
Figure 2. Fractional conversion vs time (experimental data and RPM) (a) and reaction rate r vs $(P_{\text{CO}_2}/P_e - 1)$ (b) for carbonation reaction of dolomite derived CaO under $P_{\text{CO}_2}=0.8, 1.0$ and 1.25atm and $T=850^{\circ}\text{C}$.

The activation energy used here was set equal to 20 kJ/mol and using the above results the pre-exponential factor was calculated equal to $6,9\text{E-}06 \text{ m}^4/(\text{kmol s})$ which is close to values referred in other widely accepted works ($5\text{E-}06 \text{ m}^4/(\text{kmol s})$ by Grasa and Murillo [3], $6\text{E-}06 \text{ m}^4/(\text{kmol s})$ by Bhatia and Perlmutter [5]). Thus, the reaction rate r can be calculated using the following expression:

$$r = 6.9 \cdot 10^{-6} \exp\left(-\frac{20}{RT}\right) \left(\frac{P_{\text{CO}_2}}{P_e} - 1\right)^4, \frac{\text{m}^4}{\text{kmol s}} \quad (8)$$

2. Calcination kinetics

The calcination stage analysis is very important for the heat storage application as it is needed to be conducted under high CO₂ partial pressures, and so fast kinetics are questionable. Dolomite (CaCO₃/MgO) and limestone were calcined under the same conditions of temperature and P_{CO_2} for comparison reasons. Figure 3a shows that dolomite decomposes faster than limestone, probably due to its higher initial surface area ($7.47 \text{ m}^2/\text{g}$ for dolomite and $1.19 \text{ m}^2/\text{g}$ for limestone), as it needs almost 60s to be fully calcined under 1.5 atm of P_{CO_2} and $T=950^{\circ}\text{C}$. The reaction rate is of course much faster at low CO₂ concentrations.



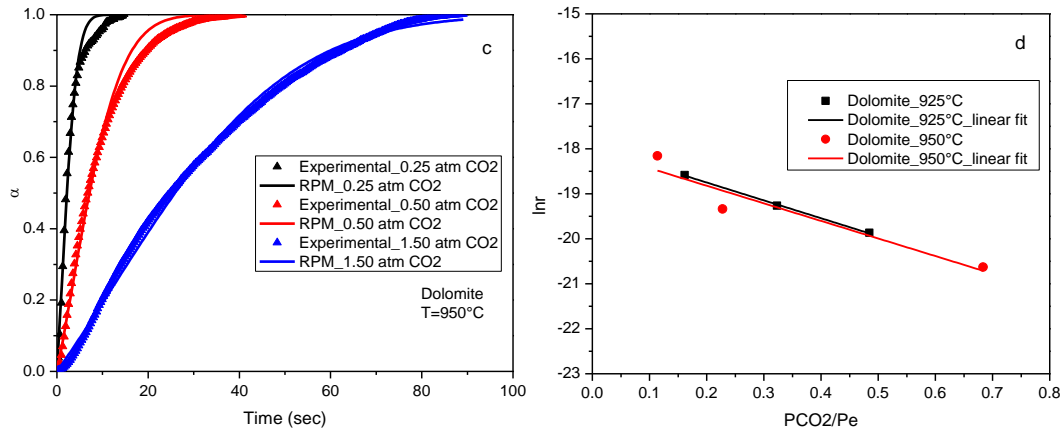


Figure 3. Fractional conversion vs time (experimental data) for calcination reaction of dolomite and limestone under $P_{CO_2}=0.25$ and 1.50 atm and $T=950^\circ\text{C}$ (a). Fractional conversion vs time (experimental data and RPM) for calcination of dolomite under $P_{CO_2}=0.25, 0.50$ and 0.75 atm and at $T=925^\circ\text{C}$ (b), calcination of dolomite under $P_{CO_2}=0.25, 0.50$ and 1.50 atm and at $T=950^\circ\text{C}$ (c) and $\ln r$ vs (P_{CO_2}/P_e) (d).

To determine the reaction order different P_{CO_2} were studied at a constant temperature. Dolomite was calcined under $P_{CO_2}=0.25, 0.50$ and 0.75 atm at 925°C and $P_{CO_2}=0.25, 0.50$ and 1.50 atm at 950°C . The RPM described adequately the experimental results under all tested conditions indicating that predicts correctly the surface area evolution during the reaction. The values of r were then plotted versus P_{CO_2}/P_e and it was found that an exponential relation is followed:

$$f(P_{CO_2}) = \exp\left(-a \frac{P_{CO_2}}{P_e}\right) \quad (9)$$

For dolomite and for the two different temperatures it was found that $\alpha=4$. Garcia-Labiano [6] found the same result providing a relatively good fitting to their experimental data. On the other hand Khinast [7], who tested calcination under low temperatures and CO_2 partial pressures found $\alpha=11$. The pre-exponential factor was calculated equal to $k_0=5.5\text{m/s}$ or $150\text{ kmol/m}^2\text{s}$ using $E_\alpha=205\text{kJ/mol}$ from the literature [8]. Summarizing, the r expression for calcination reaction transforms to:

$$r = 5.5 \exp\left(-\frac{205}{RT}\right) \exp\left(-4 \frac{P_{CO_2}}{P_e}\right), \text{ m/s} \quad (10)$$

3. Deactivation modelling

Figure 4 shows the evolution of the maximum conversion achieved through 10 successive carbonation/calcination cycles for dolomite and limestone.

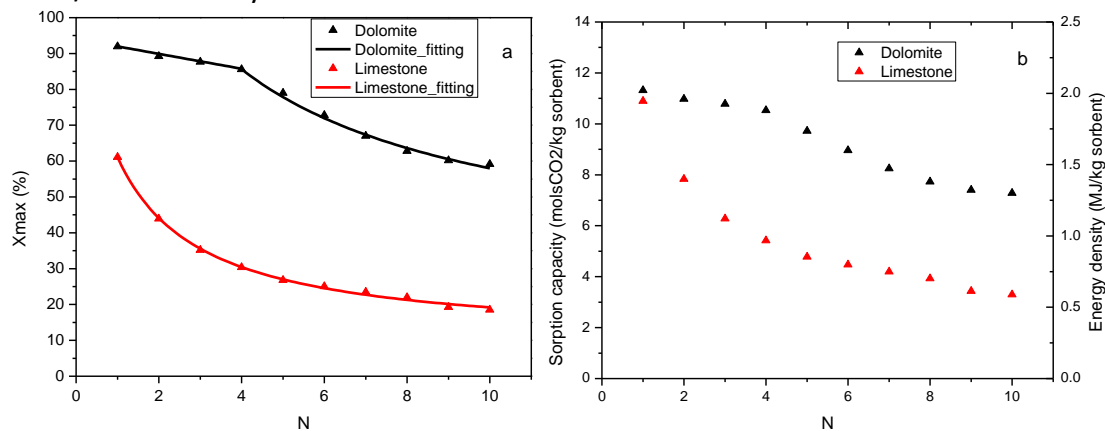


Figure 4. Evolution of maximum conversion (a) and sorption capacity/energy density (b) of limestone and dolomite through the cycles. (Carbonation: 2%Ar/ CO_2 , 850°C , 8min; Calcination: 25% CO_2/N_2 , 900°C , 8min).

Generally, dolomite attains higher maximum conversions starting from almost 95% for the 1st cycle and ending up to more than 60% during the 10th cycle. In contrary, limestone achieved 60%

in the 1st cycle and around 20% in the 10th cycle. As mentioned before, dolomite's higher conversion is attributed to its lower CaO content distributed to larger surface area than limestone, making it possible to be consumed almost totally during the surface reaction controlled regime of carbonation reaction. Regarding the fitting, eq. 7 describes well the experimental results for limestone. Dolomite exhibited two distinct regions: one linear for the first four cycles and then it also followed the same deactivation expression (eq. 7). This was probably due to separation of MgO/CaO phases after the 4th cycle as also has been observed previously [9]. The fitting parameters of eq. 7 were the deactivation rate constant k and the residual conversion X_r (Table 2). The residual conversion of dolomite is found to be three times larger than the one of limestone, while the deactivation rate constant less than half. This behaviour is attributed to MgO content that enhances the anti-sintering properties of dolomite. The linear fitting for the first four cycles follows the equation:

$$X_N = X_1 - k(N - 1), \quad \text{where } k = 2.076 \quad (11)$$

Table 2. Deactivation rate constant k and residual conversion X_r values derived from eq.7 for dolomite and limestone.

	Dolomite	Limestone
X_r (%)	29.0	9.8
k	0.24	0.59

CONCLUSIONS

Concluding, carbonation reaction was completed in less than 10 seconds for both tested materials under $P_{CO_2}=1.25$ atm and $T=850^\circ C$. Dolomite and limestone exhibited similar reaction rates during carbonation stage and the reaction was adequately modelled for both materials calculating the pre-exponential factor $k_0=6,9E-06$ m⁴/(kmol s) and finding a first order dependence on the P_{CO_2} . The same procedure for calcination reaction showed that dolomite decomposed faster than limestone owing to its higher surface area. Dolomite was fully calcined in 1.5 atm of pure CO₂ in almost 60 seconds. An exponential decay of the rate with respect to P_{CO_2} was observed, while the pre-exponential factor was found equal to 5.5 m/s. The deactivation study showed that dolomite achieved higher maximum conversions through the cycles and exhibited half the deactivation of limestone. It is concluded that dolomite is a material with high energy density and fast Ca-L reaction rates, thus appropriate for TCES applications.

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