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CFD Analysis of the CaO-CO_2 Reaction in a Thermo-Gravimetric Apparatus

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Thermo-gravimetric analysis (TGA) is a useful technique to study the kinetics of gas-solid reactions and specifically it has been widely used to investigate the carbonation reaction between carbon dioxide and calcium oxide based solid sorbents, which is the basis of a promising CCS technology. Typical conversion rates of the carbonation reaction initial fast stage measured by TGA are lower than about 0.06 s^{-1}.

However, TGA results can be significantly affected by the external mass transfer when a fast gas-solid reaction, such as the carbonation reaction, is considered, namely, when the intrinsic conversion rates are higher than 0.2 s^{-1}. In this case the conversion measurement using the thermo-gravimetric analysis may lead to inaccurate results (apparent reaction rate) if the mass transfer of the gaseous reactant is not properly accounted for. In this work a non-stationary computational fluid dynamics (CFD) study of the carbonation reaction was performed considering a horizontal TGA type, using the CFD commercial code ANSYS FLUENT® 15.0, neglecting inter-particle and intra-particle mass diffusion. A surface reaction model was assumed at the crucible surface and the conversion-time profiles were calculated varying the reactant gas flow rate.

The velocity field around and inside the crucible were computed and analyzed as well as the reactant concentration profiles, in order to evaluate the effect of the operative conditions on the reaction rate measurements.

It was found that the calculated apparent conversion rate is about 5-6 times slower than the intrinsic conversion rate due to the non-stationary carbon dioxide concentration profile established from the bulk to the crucible surface.

1. Introduction

Human activities have changed the energy budget of the Earth by introducing in the atmosphere greenhouse gases (GHGs) such as carbon dioxide. The Intergovernmental Panel on Climate Change provides a scientific demonstration of the climate change due to the GHGs emissions and, more specifically, of the carbon dioxide (Stocker, 2013). The carbon dioxide capture and storage (CCS) is one of the mitigation strategies for the atmospheric GHG reduction. Specifically, the CO_2 separation with solid sorbents is a promising technology that can be integrated with existing CO_2 emitting plants. It is based on the CO_2 carbonation reaction with calcium oxide, a fast non-catalytic gas-solid reaction that uses inexpensive solid reactants.

According to Bhatia and Perlmutter (1983), the conversion-time curves of the carbonation reaction are characterized by an initial fast chemically controlled regime followed by a slow product layer diffusion controlled stage.

The Thermogravimetric Analysis (TGA) is a widely used technique for studying the kinetics of the carbonation reaction (Barker, 1973). Typical conversion rates of the carbonation reaction initial fast stage measured by TGA are lower than about 0.06 s^{-1} (Sun et al., 2008). However, the conversion measurements of a fast gas-solid reaction, such as the carbonation, using the TGA may lead to inaccurate results if the mass transfer of the gaseous reactant is not carefully accounted for (Song et al., 2006). Recently, Biasin et al. (2015), using

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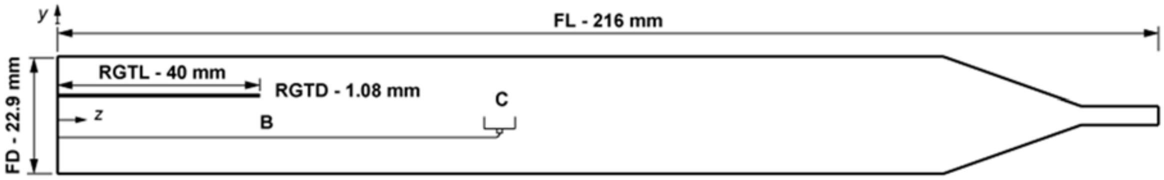


Figure 1 Geometry of the TA SDT Q600, where FD is the furnace diameter, FL is the furnace length, RTGL is the reactive gas tube length, RTGD is the reactive gas tube diameter, B is the beam of the balance and C is the crucible

synchrotron radiation in-situ XRD to investigate the carbonation reaction, measured initial conversion rates of about 0.28 s^{-1} significantly higher than the values previously obtained through TGA, and suggested that such difference could be due to the external mass diffusion affecting the thermo-gravimetric data. However, several authors, who performed TGA measurements of the carbonation reaction, claimed that their results are not limited by the external mass diffusion (Sun et al., 2008), being independent from the gas flow rate (Grasa et al., 2009). Therefore, in this work a computational fluid dynamics (CFD) study is performed on a TGA apparatus, to investigate the effect of external mass diffusion on the carbonation reaction conversion measurements by TGA. The CFD commercial code ANSYS FLUENT® 15.0 is used to perform the numerical simulations. The velocity field around and inside the crucible where the reaction occurs as well as the reactant concentration profiles are analyzed, in order to evaluate the effect of these variables on the reaction rate measurements. In this work, inter-particle and intra-particle mass transfer resistances are neglected: typically, the assumption of negligible inter-particle diffusion is experimentally satisfied by using small amounts of sample mass, while the assumption of negligible intra-particle diffusion is realized by using small particle size (less than 53-63 μm) and high carbon dioxide partial pressure (Sun et al., 2008).

2. TGA equipment

The apparatus selected for the CFD simulations of this work is the TA SDT Q600. It is a horizontal thermo-balance which is composed by several components: a balance, a heating system, a tubular furnace, a unit for the temperature measurement and a recording system. Figure 1 shows the geometry of the furnace where two crucibles are located. The reaction atmosphere is fed from the reactive gas tube (at the left of Figure 1) connected to the inert or reactive gas lines. Downstream of the crucibles the reaction chamber tapers until reaches the purge gas zone, where exhaust gases leave the reaction chamber.

2.1 Meshing

The computational domain was meshed with a hybrid mesh. Close to the furnace walls a structured mesh was imposed, whereas an unstructured mesh was used for the other parts of the domain. Specifically, tetrahedron cells were chosen and mesh refining was performed in the proximity of the sudden expansion and close to the two crucibles. The cell maximum and minimum size were set to 6 mm and to 0.3 mm, respectively. In this way, about 800,000 computational cells and 2,000,000 nodes were obtained.

3. Operative conditions

In the simulated carbonation thermo-gravimetric experiment, a small amount (5 mg) of sorbent sample (CaO) was loaded in one of the two crucibles (the crucible internal diameter is 5.5 mm). Such sample amount is small enough that inter-particle mass diffusion can be neglected (Sun et al., 2008). The simulated experiment is operated at 1 bar and at isothermal conditions (650 °C), which in a real TGA experiment are typically reached by heating the furnace in nitrogen. Therefore, in the first instants of the simulations nitrogen is fed at 650 °C.

Table 1 Gas flow regime inside the TGA furnace and the reactive gas tube at 650 °C and 1 atm.

Flow rate		Furnace			Reactive gas tube		
Normal flow rate	Effective flow rate	$\bar{v}_F$	$Re_{N_2,F}$	$Re_{CO_2,F}$	$\bar{v}_{RGT}$	$Re_{N_2,RGT}$	$Re_{CO_2,RGT}$
[Nm^3 min^{-1}]	[m^3 s^{-1}]	[m s^{-1}]	[-]	[-]	[m s^{-1}]	[-]	[-]
100	5.18×10^{-6}	0.0126	2.71	4.43	5.66	57.4	93.9
200	1.04×10^{-5}	0.0252	5.42	8.87	11.3	115	188

Afterwards, a gas switch is performed from the inert atmosphere to the reactive gas which consists of pure carbon dioxide. TGA results are commonly expressed in dimensionless form through the CaO fractional conversion as a function of time.

4. Carbonation reaction rates

The aim of the work is to investigate the influence of the external mass diffusion on the initial fast stage (controlled by the surface chemical reaction) of the carbonation. The second carbonation stage is slow and controlled by the product-layer diffusion (Bhatia and Perlmutter, 1983) and, therefore, is neglected in this work, because in this stage the external mass diffusion has no effect on the carbonation kinetics. Consequently, in this CFD study a simple reaction rate model is assumed, neglecting the product-layer diffusion, the abrupt transition between the first and second stage, and the pore closure. Additionally, the effect of the CO_2 equilibrium concentration on the reaction rate was neglected as well, because of the low temperature (650 °C). The functional form used to express the conversion rate is based on the work of Sun et al. (2008), who demonstrated with experimental results that at low CO_2 partial pressures the carbonation reaction is first order, but when the CO_2 partial pressure is higher than 10 kPa the reaction rate is zeroth order. Therefore, when the CO_2 partial pressure is higher than 10 kPa, the CaO conversion (X) rate is expressed as:

$$\frac{dX}{dt} = k_0 M_{CaO} S_0 \left(1 - X\right) = k_0^{'} \left(1 - X\right) \tag{1}$$

where k_0 is the zeroth order intrinsic rate constant, S_0 is the initial specific surface area and M_{CaO} is the CaO molecular weight, which can grouped in the constant $k_0^{'}$. This constant can be estimated from the data of Biasin et al. (2015), obtained with a technique alternative to TGA (in-situ synchrotron radiation XRD) and not affected by external mass diffusion. They measured an average initial dX / dt equal to 0.28 s^{-1} and from this value $k_0^{'}$ was estimated.

Following Sun et al. (2008), below a partial pressure of 10 kPa, the reaction order switches to first order, and, accordingly, the conversion rate is expressed as:

$$\frac{dX}{dt} = k_1^{'} C_{CO_2} \left(1 - X\right) \tag{2}$$

where $k_0^{'} = k_1^{'} C_{CO_2}^{*}$ and $C_{CO_2}^{*}$ is the concentration value when the CO_2 partial pressure is equal to 10 kPa and C_{CO_2} is the CO_2 concentration at the crucible surface. Because the inter-particle diffusion resistances are negligible, the reaction is assumed to occur at the crucible surface, where the CaO moles are expressed in terms of surface density (CaO moles loaded per unit of crucible internal bottom surface).

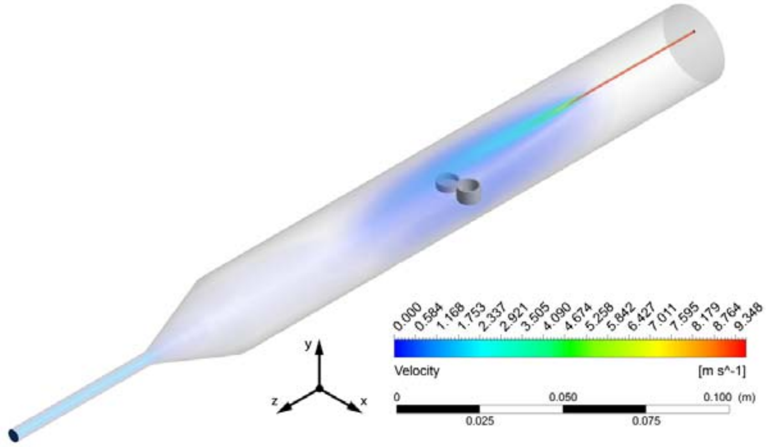


Figure 2 Three-dimensional representation of the velocity field (650 °C, 1 atm, inlet gas is CO_2 and flowrate equal to 100 NmL min^{-1})

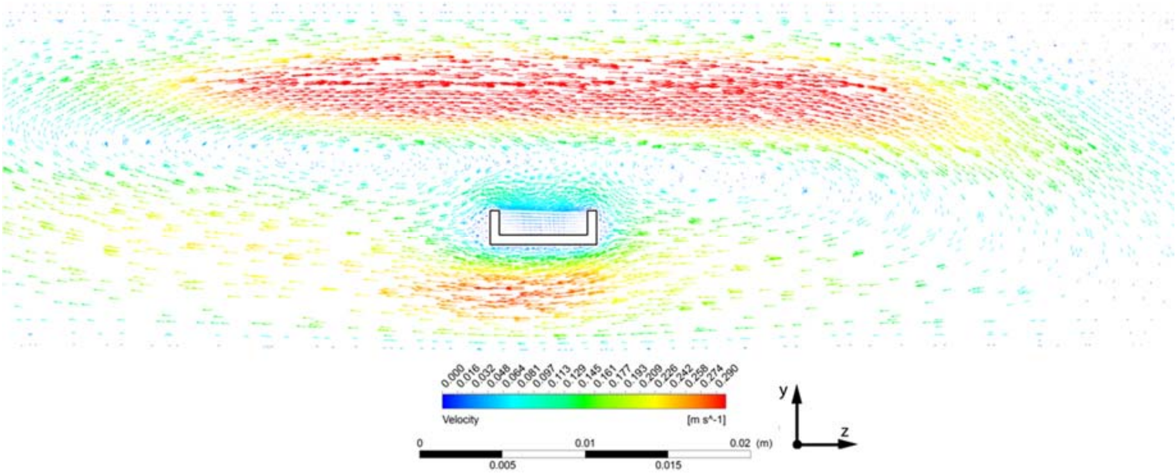


Figure 3 Predicted velocity field around and inside the crucible where reaction occurs (650 °C, 1 atm, inlet gas is CO_2 and flowrate equal to 100 NmL min^{-1})

5. TGA gas flow regime

The numerical simulations were performed with gas flow rates equal to 100 and 200 NmL min^{-1}. The gas fed is initially pure N_2, which is afterwards switched to pure CO_2. Based on these operative conditions, the Reynolds number was calculated both for the furnace and the reactive gas tube. The definition of the Reynolds number employed for cylindrical pipes is $Re_{i,j} = \rho_i \bar{v}_j d_j / \mu_i$ where i refers to N_2 or CO_2, j to the reactive gas tube or to the furnace, ρ is the density of species *i*, $\bar{v}_j$ is the average gas velocity inside *j*, d_j is the diameter, μ_i is the viscosity of the gaseous species *i*. The results are listed in Table 1, which shows that the gas flow regime is laminar ($Re_{i,j} \leq 2100$) both in the furnace and in the reactive gas tube.

6. Results

The output of the CFD simulations consist of the velocity field and the CO_2 concentration field inside the TGA (TA SDT Q600), and the conversion-time curves.

6.1 Velocity field

Figure 2 shows the three-dimensional velocity field inside the furnace (for 100 NmL min^{-1}). A detailed view of the velocity field around and inside the reaction crucible (the crucible where the CaO sample is loaded and the reaction occurs) is shown in Figure 3. Since the effective cross section of the furnace is reduced due to the presence of the two crucibles, the flow accelerates and the velocity increases above the crucibles, as shown in Figure 3. The gas velocity is considerably small (much smaller than in the bulk) inside the crucible.

6.2 Carbon dioxide concentration field

When the gas flow is switched from N_2 to CO_2, an axial carbon dioxide profile is established due to CO_2 convection and diffusion. Figure 4 shows the CO_2 reactant front at the first instants after the gas switch. The surface of the crucible is progressively reached by CO_2 whose concentration gradually increases, as represented in Figure 5b.

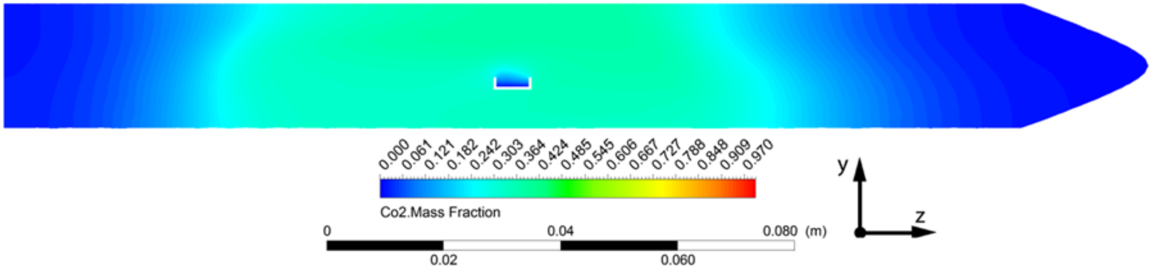
6.3 Surface reaction

The carbonation reaction occurs at the surface of the smaller crucible according to Eqs. (1) and (2). The results of the numerical simulations, in terms of conversion vs time, are reported in Figure 5a which shows the apparent reaction rates computed from the CFD output, compared to the solution of Eq. (1) that represents the intrinsic reaction rate when the reaction surface is exposed to the bulk concentration value. This trend of the apparent reaction rate is clearly due to the CO_2 mole fraction profile at the reaction surface (Figure 5b).

(a) 1 s.

(b) 2s.

(c) 3s.



(d) 5s.

Figure 4 Contours of the CO_2 mass fraction in the first seconds of the simulations (650 °C, 1 atm, inlet gas is CO_2 and flowrate equal to 100 NmL min^{-1})

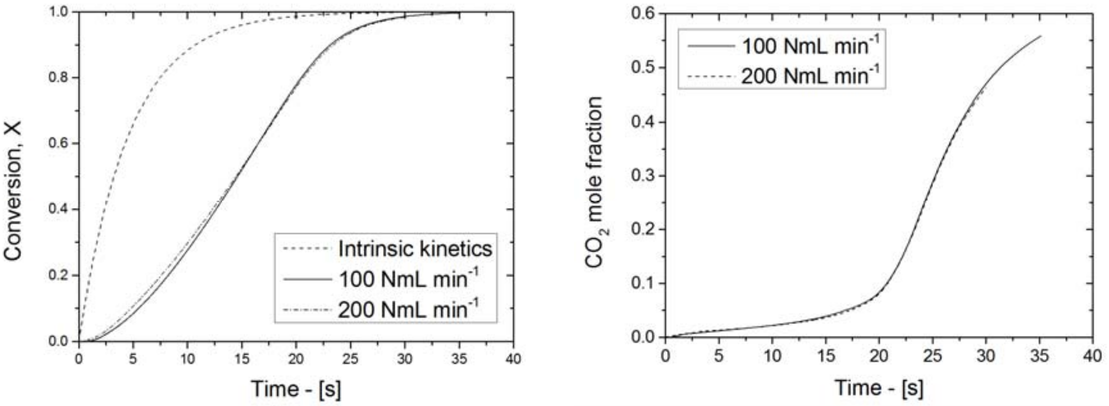
The CO_2 mole fraction vs time curve is the result of the balance between the incoming CO_2 from the bulk flow and the reactant consumption due to the carbonation. This CO_2 mole fraction profile cannot be predicted without a CFD simulation and the assumption of constant CO_2 concentration at the reaction surface (equal to the bulk concentration) is clearly inaccurate for the initial fast regime of the CaO carbonation.

The simulation results provide an apparent reaction rate that depends significantly on the external mass transfer. Specifically, the conversion-time curve based on the intrinsic reaction rate has an initial slope of 0.28 s^{-1} whereas at 100 and 200 NmL min^{-1} the apparent conversion rate has a maximum slope of about 0.05 s^{-1}. It is noteworthy that such value of apparent conversion rate is quantitatively in agreement with the typical values obtained experimentally from TGA measurements (Sun et al., 2008).

7. Conclusions

In this work, CFD simulations of a typical CaO carbonation experiment in a horizontal TGA (TA SDT Q600) were performed to investigate the influence of the external mass transfer on the conversion data obtained through TGA.

Several results were obtained from the CFD simulations. The first is that the gas velocity field inside the TGA furnace, especially around and inside the crucible, is complex and the velocity inside the crucible is very low compared to the bulk velocity. Consequently, when the gas flow switches from the inert gas (N_2) to the reactant (CO_2), at the reaction surface the CO_2 concentration gradually increases up to reaching the bulk concentration, but most of the reaction occurs with a reactant concentration significantly lower than the bulk concentration. Finally, the apparent conversion-time curve (computed as output of the CFD simulations) are significantly different from the curves obtained from the intrinsic reaction rate due to the non-stationary local carbon dioxide concentration profiles. Specifically, the intrinsic conversion rates are about 5-6 times higher the apparent conversion rates (computed from the CFD simulations), thus demonstrating that TGA measurements of the carbonation reaction are strongly affected by the external mass transfer. It is noteworthy that the values of the computed apparent conversion rate are quantitatively in agreement with the typical values obtained experimentally in TGA measurements of the carbonation reaction.



(a) Conversion vs time curves

(b) CO_2 mole fraction vs time

Figure 5 Simulation results of the conversion-time curves and of the (surface averaged) CO_2 mole fraction at the reaction surface (650 °C, 1 atm, inlet gas is CO_2)

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