Modeling dry-scrubbing of gaseous HCl with hydrated lime in cyclones with and without recirculation

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ABSTRACT

A mathematical model describing the dry-scrubbing of gaseous hydrogen chloride (HCl) with solid hydrated lime particles ($Ca(OH)_2$) was developed and experimentally verified. The model applies to cyclone systems with and without recirculation, where reaction and particle collection occurs in the same processing unit. The Modified Grain Model was selected to describe the behavior of the reaction process and it was assumed that the gas and the solid particles flow in the reactor with a plug flow. In this work, this behavior is approximated by a cascade of N CSTRs in series. Some of the model parameters were estimated by optimization taking into account the experimental results obtained. A good agreement was observed between the experimental results and those predicted by the model, where the main control resistance is the diffusion of the gaseous reactant in the layer of solid product formed.

1. Introduction

In today's industrialized society the design of control equipment must include the environmental component as one of main design goals. Software simulation and optimization methods based on process models can be valuable tools in order to support industrial engineers in the design of optimized air pollution control equipment.

Many chemical and metallurgical industrial processes (e.g. extraction and reduction of ores, combustion of solids, incineration of solid wastes, removal of pollutants in gaseous emissions, . . .) involve heterogeneous reactions. Non-catalytic gas–solid reactions comprise a significant fraction of heterogeneous reactions. These have received considerable attention resulting in many models and techniques in order to describe and understand them.

Porous materials are commonly used as solid reactants since normally they have specific surface areas much larger than those observed in non-porous solids. In non-catalytic gas–solid reactions involving porous materials, significant structural changes usually occur in the solid reactant as the reaction progresses. The changes are mainly caused by the difference between the molar volumes of

solid reactant and the product of the reaction and therefore both the porosity of the solid reactant and the diffusivity of gaseous reactants through the porous matrix will change with the progress of the reaction [1,2].

It is usual in these reactions processes to describe the solid reactant as formed by solid particles, clusters of small non-porous grains of different sizes. The reaction occurs in the grains involving physical, chemical and thermal phenomena. If the reaction product is solid, it will form a solid at the surface of the grains and thus an additional diffusion resistance is introduced as the reaction progresses. When the molar volume of the reaction product is higher than that of the solid reactant, an increase in grain size occurs. In general the most reacted grains, which are located at the boundary of the particle, are larger than those within it and thus hinder the diffusion of the gaseous reactant [3]. In some cases blocking of pores may occur and consequently the reaction ends before complete conversion of the solid reactant [3,4]. This phenomenon has been reported in the literature as the reaction *die-off* [3]. Based on the initial porosity of the solid reactant and the ratio of molar volumes of solid reactant and product, it is possible to predict the maximum reactant conversion [2].

The complexity and variety of phenomena involved in these reaction processes explains how it can be difficult to develop a model capable of simulating the reaction behavior [5]. A good model must be able to provide a good interpretation of the experimental behavior, and in particular of the structural changes occurring in the solid reactant. It must predict the rate-controlling mechanism(s) and the gas and solid conversions for different oper-

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Nomenclature

A, B	gas and solid reactant, respectively
C_A	HCl concentration (mol m^{-3})
CSTR	continuously stirred tank reactor
D	solid product formed
d_{ng}	debit of solid reactant (grains s^{-1})
def	effective diffusion coefficient of the gaseous reactant in the pores of particle solid reactant (m^2 s^{-1})
dif	effective diffusion coefficient of the gaseous reactant in the layer of solid product formed (m^2 s^{-1})
f_{cap}	solid fraction captured between CSTRs that is unavailable to continue to react
f_{obj}	objective function
f_r	recirculation fraction on ReCyclone systems
K	global mass transfer resistance of the reaction process (s m^{-3})
k_s	kinetic constant (m s^{-1})
M_B	molar mass of the solid reactant (kg kmol^{-1})
n_B	molar flow rate of solid reactant (mol s^{-1})
N	number of CSTRs in series
$N_{exp.}$	number of experimental data
n_g	quantity of solid reactant available for reaction (number of grains)
Q	total gas flow rate (N m^3 s^{-1})
RC	ReCyclone system
R/SR	ratio between the amount of solid reactant and gaseous reactant at the inlet of the reaction system (R) and that corresponding to the stoichiometric quantity (SR)
$-r_A$	rate of consumption of the gaseous reactant (mol s^{-1})
$-r_B$	rate of consumption of the solid reactant (mol s^{-1})
R	radius (m)
$St\ HE$	modified Stairmand high efficiency cyclone
tr	mean residence time (s)
V	useful volume in the reaction systems (m^3)
$\dot{W}_B$	mass flow rate of solid reactant (kg s^{-1})
X	solid reactant conversion based on fresh molar flow rate of solid reactant (%)

Greek symbols

α	ratio of the molar volumes of the solid product formed to the solid reactant
ρ_B	specific gravity of the solid reactant (kg m^{-3})
ε_s	porosity of the solid reactant
ε_{s_0}	initial porosity of the solid reactant
$\eta_{capt.tot.}$	average particle collection efficiency (%)
$\eta_{f_{cap}}$	solid capture efficiency in each CSTR (%)
η_{HCl}	HCl removal efficiency (%)
τ	time constant (s)

Subscripts

c	unreacted core
cc	cyclone concentrator
cr	cyclone reactor
g	grain
gas	gas
in	inlet
max	maximum
min	minimum
mod	model
out	outlet
p	pellet
r	outer radius
rea	react
$sol.$	solid
RS	reaction system

ating conditions. In some cases it should have features that allow its incorporation into models of reactors or processes.

The models that have been proposed to describe the non-catalytic gas–solid reactions can be classified into different categories according to the surface where the reaction starts and the diffusion characteristics of the gaseous reactant [6–8] as: *Sharp Interface Model* or *Unreacted Shrinking Core Model*, *Volume* or *Homogeneous Reaction Models*, *Particle-Pellet Model* or *Grain Models* and *Pore Models*.

An important application of gas–solid reactions, still receiving most of the attention, is the adsorption/absorption of acid gases (in particular HCl and SO$_2$) in a solid reactant (mainly calcium or sodium compounds). These systems are used for the treatment of gaseous emissions from the processes of incineration of municipal solid waste and wastes containing chlorine. The reaction is a non-catalytic gas–solid reaction characterized by the gradual decrease in porosity of the solid reactant and hence, pore blockage may occur.

The Grain Model has been extensively used to describe the behavior reaction between acid gases and solid reactants [9–11]. This model is particularly useful when the solid reactant is composed of small grains and the grains retain their original size during the reaction. However, in cases where changes in the structure of the solid reactant occur, the model is unsatisfactory and, in general, overestimates the final reactant conversion [3]. Accordingly, to take into account the structural changes observed in the solid reactant, many authors [2,3,12–14] have used the *Modified Grain Models*.

In this work the *Modified Grain Model* was selected. This model is relatively simple and widely used in the literature to describe such reactions, and there are similarities between the assumptions of this model and the physical reality of the reaction system under study. Observations by electron microscopy and the characterization of the porous structure of particles of Ca(OH)$_2$ used in this study showed, precisely, that there are clusters of grains hardly porous [15].

The aim of the present paper is to predict the HCl removal efficiency and the conversion of the hydrated lime, Ca(OH)$_2$, based on the developed model (integrating the *Modified Grain Model*) when cyclones are used as reactors, namely a modified Stairmand HE cyclone (St He) and two ReCyclone systems (RC), comprising two different sized optimized cyclones (0.02 and 0.026 m internal diameter) [16]. The model will be applied to the experimental results of Chibante et al. [17,18].

2. Model description

Consider the general form of a gas–solid non-catalytic reaction as follows:

$$aA(g) + bB(s) \rightarrow dD(s)$$
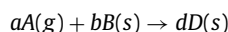
Gas *A* diffuses and reacts with porous solid *B* to produce a solid product *D*.

The major rate-limiting steps are: (i) transfer of the external gas reactant to the pellet surface; (ii) diffusion of the gas through the intergranular pores; (iii) chemical reaction within the solid phase; and (iv) diffusion of the gas through the product layer formed [5]. Accordingly, the reaction process may take place only on chemical regime control (chemical reaction itself controls the overall kinet-

ics) or diffusion control (the transfer of mass and/or the diffusion of the gas either in the pores or in the layer of the solid product formed is the control step). Other possibilities are mixed regimes corresponding to various combinations of the controlling steps.

In our previous work [9] it was concluded that the external mass transfer resistance is not the rate-limiting step in the present operating conditions because of the high velocities of the gas achieved in the cyclone reactor. To evaluate the importance of the internal mass transfer resistance, the effective diffusivity of HCl in the pores of the solid reactant has been estimated using the *Dusty Gas Model* [19], using the Weisz–Prater [20] criteria. The conclusions of this test were that the internal mass transfer limitations can be neglected before the product layer formed. However, considering that the solid product formed is $CaCl_2 \cdot 2H_2O$, the molar volume of the product formed is higher than that of the solid reactant ($Ca(OH)_2$) leading to an increase in grain size and hence an increase in that resistance.

The resistance to diffusion of the gas in the layer of solid product formed should have a key role in the course of the experiment, since the effective diffusivities associated with this reaction process are generally lower than the reaction rate.

In this context, it is expected that the reaction under study can be described by a combination of resistances, which occur either at the grain level (chemical reaction and diffusion of HCl in the layer of solid product formed) and at the particles' level (diffusion of HCl in the solid reactant pores).

The reaction modeling of the phenomenon at particle and grain levels leads to a non-linear system of coupled partial differential equations, which requires high computational times to obtain an analytical solution [12,21] or even no solution [21] and thus it is usually necessary to use approximate numerical solutions. As the maximum solid conversion reached experimentally was of the order of 30%, and as the solid reactant used was mainly composed of macro-pores [15], the developed model only considers the reaction phenomenon at grain level. Thus, the model includes the resistances related to the chemical reaction and the diffusion of HCl in the layer of solid product. The resistance to diffusion of HCl in the pores of the solid reactant has been neglected. However, the change in the diffusion coefficient due the porosity decrease of the solid reactant with the progress of the reaction will also be discussed.

2.1. Model main assumptions

The following major assumptions are introduced to derive the basic equations:

- Pseudo-steady-state approximation;
- The reaction takes place under isothermal conditions and at constant pressure;
- The reaction is irreversible and first order with respect to the gaseous reactant;
- The pellet retains its spherical shape and its initial size ($R_p = 1.5 \times 10^{-5}$ m) in course of the reaction. The grains are non-porous and retain its spherical shape but increase its initial size ($R_g = 1.5 \times 10^{-7}$ m) with the reaction progress, due to the differences in the molar volume of the reaction product and solid reactant;
- The effective gaseous diffusivity through the product layer formed around the grains is constant.

2.2. Model equations

2.2.1. Recirculating cyclones (ReCyclone systems)

Recirculating cyclones (RC) combine a numerically optimized reverse-flow gas cyclone [16], called Hurricane, with a straight-through cyclone concentrator. These systems are called ReCyclone
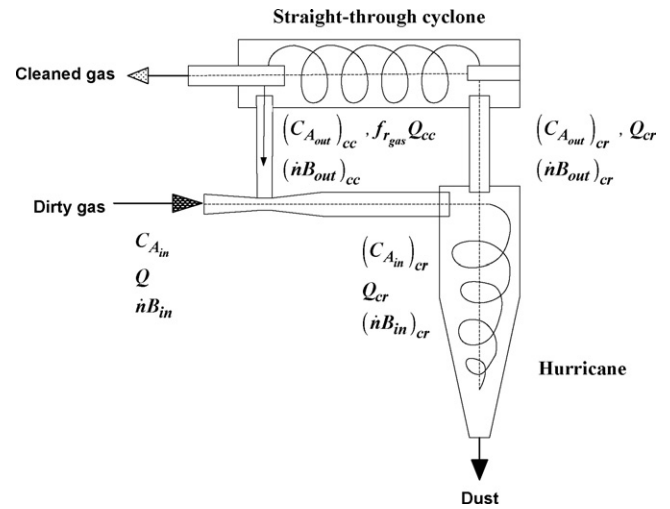

Fig. 1. Schematic flow diagram for the dry-scrubbing in a ReCyclone system.

systems, where the concentrator promotes the partial recirculation of the gas and solids by some means, such as by a venturi at laboratory scale or by a blower or ejector at industrial-scale. In these systems the reactor is the reverse-flow cyclone, which is also the only particle collector. However at the exit of the reactor some solid may remain unreacted or partially reacted and acid reactant may still be present for the reaction to proceed in the cyclone concentrator. Thus, the modeling of the reaction process in these systems should include both the reverse-flow cyclone and the cyclone concentrator.

Fig. 1 shows a schematic flow diagram of the dry-scrubbing in ReCyclone systems, where the cyclone reactor and the cyclone concentrator can be distinguished. Moreover, some flow rates and concentrations are also included.

2.2.1.1. Optimized cyclone (Hurricane).
Due to the partial recirculation of the gas and solids, the solid reactant, the gas and the acid flow rates into the cyclone reactor are different from those fed to the ReCyclone system.

Thus, at the inlet of the cyclone reactor the HCl concentration $\left[(C_{A_{in}})_{cr} \right]$ depends on the recirculation gas fraction to the cyclone reactor $(f_{r_{gas}})$, the HCl concentration at the inlet of the ReCyclone $(C_{A_{in}})$ and the HCl concentration at the outlet of the cyclone concentrator $\left[(C_{A_{out}})_{cc} \right]$ through the following relationship:

$$\left(C_{A_{in}} \right)_{cr} = \left(1 - f_{r_{gas}} \right) C_{A_{in}} + f_{r_{gas}} \left(C_{A_{out}} \right)_{cc} \tag{1}$$

The gas flow rate at the inlet of the cyclone reactor (Q_{cr}) depends on the gas flow rate at the inlet of the ReCyclone (Q) and $f_{r_{gas}}$ as follows:

$$Q_{cr} = \frac{Q}{1 - f_{r_{gas}}} \tag{2}$$

At the inlet of the cyclone reactor the molar flow rate of the solid reactant $\left[(\dot{n}_{B_{in}})_{cr} \right]$ and its debit (number of grains per unit time) $\left[(d_{ng_{in}})_{cr} \right]$ will be dependent on either the recirculation solid fraction ($f_{r_{sol.}}$), the inlet molar flow rate ($\dot{n}_{B_{in}}$) or the inlet debit ($d_{ng_{in}}$) verified at the inlet of the ReCyclone and the outlet molar flow $\left[(\dot{n}_{B_{out}})_{cc} \right]$ or the outlet debit $\left[(d_{ng_{out}})_{cc} \right]$ at the cyclone concentrator by Eqs. (3) and (4).

$$\left(\dot{n}_{B_{in}} \right)_{cr} = \dot{n}_{B_{in}} + \left(\dot{n}_{B_{out}} \right)_{cc} f_{r_{sol.}} \tag{3}$$

$$\left(d_{ng_{in}} \right)_{cr} = d_{ng_{in}} + \left(d_{ng_{out}} \right)_{cc} f_{r_{sol.}} \tag{4}$$

where $d_{ng_{in}}$ is determined by:

$$d_{ng_{in}} = \dot{n}_{B_{in}} M_B \frac{1}{\rho_B} \frac{1}{(4/3)\pi \left(R_g^3\right)_{cr}} \tag{5}$$

where ρ_B and M_B are, respectively, the density and the molar mass of the solid reactant and $(R_g)_{cr}$ is the average radius of the grains at the inlet of the cyclone reactor. At the inlet of the cyclone reactor, the mixture of fresh solid reactant with partially converted solid occurs, leading to the existence of grains with radius between R_g and $(R_c)_{cc}$. A simple way to account this is to determine the radius of the grains corresponding to the weighed average, based on the two currents that mix. Thus, $(R_g)_{cr}$ is calculated by:

$$(R_g)_{cr} = \left[\left(\dot{n}_{B_{in}}\right)_{cr} M_B \frac{1}{\rho_B} \frac{1}{(4/3)\pi \left(d_{ng_{in}}\right)_{cr}} \right]^{1/3} \tag{6}$$

where $\left(\dot{n}_{B_{in}}\right)_{cr}$ and $\left(d_{ng_{in}}\right)_{cr}$ are calculated by Eqs. (3) and (4), respectively.

Mass balance for the solid and gas phases. In accordance with our previous studies [15] it was assumed that the solid particles and the gas, flow in the cyclone reactor with a plug flow. The solid particles are captured along the cyclone, resulting in a decrease in the solid concentration along its axial length. It is still unknown how solid particles are captured along the cyclone length and if after their capture, they remain available to react in whole or in part. This behavior was simulated by representing the solids' flow by a cascade of N CSTRs in series and considering that a fraction of the solid for which the reaction ends will be captured between the outlet of each CSTR and the inlet of the one immediately following it (f_{cap}).

The solid's capture efficiency in each CSTR $\left(\eta_{f_{cap}}\right)$ is defined as the ratio between the captured mass at every unit of time and the solid mass flow rate throughout the CSTR. It is also assumed that $\eta_{f_{cap}}$ remains constant along the cyclone regardless of the axial position. Taking into account the average particle collection efficiency for the cyclone reactor $[(\eta_{cap.tot.})_{cr}]$ obtained experimentally, the value of $\eta_{f_{cap}}$ was derived from the following expression:

$$\eta_{f_{cap}} = 1 - [1 - f_{cap}(\eta_{cap.tot.})_{cr}]^{1/N_{cr}} \tag{7}$$

where N_{cr} is the number of CSTRs considered in the cyclone reactor.

A material balance to the solid reactant in the ith CSTR leads to the equation:

$$\left(\dot{n}_{B_{in}}\right)_i = \left(\dot{n}_{B_{out}}\right)_i + (-r_B)_i \tag{8}$$

where $\left(\dot{n}_{B_{in}}\right)_i$ and $\left(\dot{n}_{B_{out}}\right)_i$ are, respectively, the molar flow rate of B at the inlet and at the outlet of this CSTR and $(-r_B)_i$ is the rate of consumption of the solid reactant, which is half that of the gaseous reactant (A).

Taking into consideration the present reaction process and the *Modified Grain Model*, the molar reaction rate based on the gaseous reactant $(-r_A)_i$, is dependent on the resistance(s) considered and is of type:

$$(-r_A)_i = 4\pi \frac{(C_{A_{out}})_i}{K_i} (n_g)_i \tag{9}$$

where $(C_{A_{out}})_i$ is the acid concentration at the outlet of the ith CSTR, K_i is the global mass transfer resistance and $(n_g)_i$ is the quantity (number of grains) of B available for reaction in the ith CSTR, estimated by considering the average contact time between the gas and the solid particles in each CSTR (tr_{cr}/N_{cr}). Here tr_{cr} is the mean residence time for the gas in the cyclone reactor, determined by the ratio between the cyclone reactor volume (V_{cr}) and the gas flow through it (Q_{cr}).

For the 1st CSTR the quantity of B is given by:

$$(n_g)_1 = \left(d_{ng_{in}}\right)_{cr} \frac{tr_{cr}}{N_{cr}} \tag{10}$$

where $\left(d_{ng_{in}}\right)_{cr}$ is obtained from Eq. (4).

For the other CSTRs and considering that between CSTRs a given fraction of solid particles is unavailable for reaction, the quantity of B available to react is calculated by:

$$(n_g)_i = (n_g)_{i-1} \left(1 - \eta_{f_{cap}}\right) \tag{11}$$

The global mass transfer resistance (K_i) is a function of the resistance(s) considered. If the process is on chemical control:

$$K_i = \frac{1}{k_s(R_c^2)_i}, \tag{12}$$

If it is under diffusion control (layer of solid product formed):

$$K_i = \frac{1}{dif} \left(\frac{1}{(R_c)_i} - \frac{1}{(R_r)_i} \right) \tag{13}$$

Considering both resistances in series K_i is given by:

$$K_i = \frac{1}{k_s(R_c^2)_i} + \frac{1}{dif} \left(\frac{1}{(R_c)_i} - \frac{1}{(R_r)_i} \right) \tag{14}$$

where $(R_r)_i$ and $(R_c)_i$ are, respectively, the outer radius of the grains and the radius of unreacted core in the grains at the ith CSTR and k_s, dif are, respectively, the kinetic constant and the effective diffusion coefficient of A in D.

As the reaction proceeds there is a variation (increase) in the radius of the grain, because the molar volume of the reaction product (D) is higher than the solid reactant (B). The outer radius of the grains is then given by:

$$(R_r)_i = [\alpha(R_g^3)_{cr} + (1 - \alpha)(R_c^3)_i]^{1/3} \tag{15}$$

where α is the ratio of the molar volumes of D to B, and for the reaction under study takes the value of 2.37 [9,22], where $(R_g)_{cr}$ is determined by Eq. (6).

As with the radius of the grains, the radius of the unreacted core in the grains (R_c), i.e., the radius of B in each grain that has not reacted, varies along the reaction (decreases) and can be accounted for:

$$(R_c)_i = (R_c)_{i-1} \left(\frac{\dot{n}_{B_{out}}}{\dot{n}_{B_{in}}} \right)_i^{1/3} \tag{16}$$

For the 1st CSTR, $(R_c)_1 = (R_g)_{cr}$.

Thus, the molar flow rate of B at the exit of the ith CSTR can be obtained through:

$$\left(\dot{n}_{B_{out}}\right)_i = \left(\dot{n}_{B_{in}}\right)_i - 2\pi \frac{(C_{A_{out}})_i}{K_i} (n_g)_i \tag{17}$$

So, the molar flow rate of B that reacts in each CSTR $(\dot{n}_{B_{rea}})_i$ is the difference between the molar flow rates of B at the inlet and outlet of that particular CSTR:

$$(\dot{n}_{B_{rea.}})_i = \left(\dot{n}_{B_{in}} - \dot{n}_{B_{out}}\right)_i \tag{18}$$

Between the outlet of each CSTR and the inlet of the one immediately following it a given fraction of the solid reactant is unavailable to react, so at the inlet of the $i+1$ CSTR there will be a molar flow rate $\left[\left(\dot{n}_{B_{in}}\right)_{i+1}\right]$ and a quantity $[(n_g)_{i+1}]$ of B given by:

$$\left(\dot{n}_{B_{in}}\right)_{i+1} = \left(\dot{n}_{B_{out}}\right)_i \left(1 - \eta_{f_{cap}}\right) \tag{19}$$

and

$$(n_g)_{i+1} = (n_g)_i \left(1 - \eta_{f_{capt}}\right) \tag{20}$$

The molar flow rate of B at the outlet of the last CSTR of the cyclone reactor (N_{cr}), after solid capture $\left[\left(\dot{n}_{B_{in}}\right)_{N_{cr}+1}\right]$, may or may not correspond to the molar flow rate of this reactant that escapes the cyclone reactor, depending on whether f_{cap} is equal to 1 or not. Thus, the molar flow rate of B that escapes the cyclone reactor $\left[\left(\dot{n}_{B_{out}}\right)_{cr}\right]$ and continues to react in the cyclone concentrator is calculated by:

$$\left(\dot{n}_{B_{out}}\right)_{cr} = \left(\dot{n}_{B_{in}}\right)_{N_{cr}+1}[1 - (1 - f_{cap})(\eta_{capt.tot.})_{cr}] \tag{21}$$

The same will happen with the quantity of B that escapes the cyclone reactor and is given by:

$$\left(n_{g_{out}}\right)_{cr} = (n_g)_{N_{cr}+1}\left[1 - (1 - f_{cap})(\eta_{capt.tot.})_{cr}\right] \tag{22}$$

The material balance equations of the solid reactant (B) in the cyclone reactor that is given above must be combined with a balance of the gaseous reactant (A) to complete the proposed model since the variable $\left(C_{A_{out}}\right)_i$ appears in Eq. (17).

The equation describing the mass balance of the gaseous reactant in the ith CSTR takes the form:

$$Q_{cr}\left(C_{A_{in}}\right)_i = Q_{cr}\left(C_{A_{out}}\right)_i + (-r_A)_i \tag{23}$$

where Q_{cr} is the total gas flow rate at the inlet of the cyclone reactor [Eq. (2)], $(-r_A)_i$ is the reaction rate and $\left(C_{A_{in}}\right)_i$, $\left(C_{A_{out}}\right)_i$ are the HCl concentrations at the inlet and at the outlet of the ith CSTR, respectively.

Replacing the reaction rate $[(-r_A)_i]$ given by Eq. (9) in the previous equation, and $\left(C_{A_{out}}\right)_i$ in the equation of the material balance of the solid reactant [Eq. (17)] and knowing that $((R_c)_i/(R_c)_{i-1})^3 = (\dot{n}_{B_{in}}/\dot{n}_{B_{out}})_i$ [Eq. (16)] results:

$$(R_c)_i^3 - (R_c)_{i-1}^3 + \frac{2\pi\left(C_{A_{ent.}}\right)_i Q_{cr}(n_g)_i(R_c)_{i-1}^3}{Q_{cr}K_i\left(\dot{n}_{B_{ent.}}\right)_i + 4\pi(n_g)_i\left(\dot{n}_{B_{ent.}}\right)_i} = 0 \tag{24}$$

where $(R_c)_i$ is the only unknown variable.

Brent's method [23] was used to determine the root of Eq. (24), which ensures convergence if the root is contained in an initially arbitrated interval. The lower limit of this variable is the minimum radius that can reach the core in the grains $\left(R_{c_{min.}}\right)$ (Appendix A) and the upper limit is the radius of the grains at the inlet of the cyclone reactor $[(R_g)_{cr}]$.

2.2.1.2. Cyclone concentrator.
The cyclone concentrator is a straight-through cyclone, where a fraction of the flow of gas and solids at the exit of this is recirculated to the cyclone reactor (Hurricane) and the other fraction will exit the ReCyclone system.

The flow rates of solid and gas at the inlet of this cyclone is the same verified at the exit of the cyclone reactor. Therefore, at the inlet of the concentrator the molar flow rate $\left[\left(\dot{n}_{B_{in}}\right)_{cc}\right]$ and a quantity $\left[\left(n_{g_{in}}\right)_{cc}\right]$ of B are equal to $\left(\dot{n}_{B_{out}}\right)_{cr}$ [Eq. (21)] and $\left(n_{g_{out}}\right)_{cr}$ [Eq. (22)], respectively. In turn, the HCl concentration $\left(C_{A_{in}}\right)_{cc}$ and the gas flow (Q_{cc}) is equal to $\left(C_{A_{out}}\right)_{cr}$ [Eq. (23) when $i=N_{cr}$] and Q_{cr} [Eq. (2)], respectively.

Assuming that in the cyclone concentrator the gas and the solid flows are well described by plug flow, the same cascade of CSTRs placed in series used in the cyclone reactor will be considered here, except the fact that solid capture does not occur. Thus, the variation of the HCl concentration, the molar flow rate and the quantity of B in this cyclone are determined in the same way as in the cyclone reactor (Equations (23), (17) and (11) considering $\eta_{f_{cap}} = 0$, respectively). The quantity (number of grains) of B available to react in

the 1st CSTR is given by:

$$(n_g)_1 = \frac{\left(n_{g_{out}}\right)_{cr}}{N_{cc}} \tag{25}$$

where N_{cc} is the number of CSTRs in the cyclone concentrator.

At the exit of the cyclone concentrator there occur the same conditions found at the exit of the last CSTR in the concentrator for the gas and the solid flows, since the solid is not captured in this cyclone. At the exit of the cyclone concentrator the debit of B is:

$$\left(d_{n_{g_{out}}}\right)_{cc} = \left(n_{g_{out}}\right)_{cc}\frac{N_{cc}}{tr_{cc}} \tag{26}$$

where tr_{cc} is the average residence time of the gas in the cyclone concentrator, which is determined by the ratio between the cyclone concentrator volume (V_{cc}) and the gas flow through it (Q_{cc}).

2.2.2. Cyclones without recirculation
The reaction systems without recirculation, including the modified Stairmand HE cyclone tested, are cyclones that do not incorporate the cyclone concentrator.

Modeling of those cyclones is similar to cyclones with recirculation but taking into account that $f_{r_{gas}} = f_{r_{sol}} = 0$, so at the inlet of the cyclone reactor there is only fresh flows for the solid reactant (B) or for the gaseous reactant (A). The outlet of that reaction system is equal to the outlet of the cyclone reactor.

2.2.3. Solid reactant conversion and acid removal efficiency
The solid reactant conversion, based on fresh molar flow rate of solid reactant (at the inlet of the reaction system), predicted by this model (X_{RS_mod}), can be obtained through the ratio between the molar flow rate of B that reacted in the reaction system, which was captured in the reaction system, and the molar flow rate of B fed to the reaction system.

The HCl removal efficiency for the reaction systems predicted by this model $\left(\eta_{HCl_{RS\_mod}}\right)$ is obtained by the ratio between the quantity of HCl that reacted in the reaction system and the HCl concentration at the inlet of the reaction system.

So, when the reaction system is a RC the solid reactant conversion predicted by the model (X_{RC_mod}) is determined by the following equation:

$$X_{RC\_mod} = \frac{\left[\sum_{i=1}^{N_{cr}}(\dot{n}_{B_{rea}})_i + \sum_{i=1}^{N_{cc}}(\dot{n}_{B_{rea}})_i\right](\eta_{capt.tot.})_{RC}}{\dot{n}_{B_{in}}} \tag{27}$$

where the term $\left[\sum_{i=1}^{N_{cr}}(\dot{n}_{B_{rea}})_i\right]$ corresponds to the total molar flow rate of B that reacted in the cyclone reactor, $\left[\sum_{i=1}^{N_{cc}}(\dot{n}_{B_{rea}})_i\right]$ is the same molar flow but now in the cyclone concentrator, $(\eta_{capt.tot.})_{RC}$ is the average particle collection efficiency for the RC and $\dot{n}_{B_{in}}$ the molar flow rate of B at the inlet of the RC.

The HCl removal efficiency for the RC predicted by this model $\left(\eta_{HCl_{RC\_mod}}\right)$ is obtained through:

$$\eta_{HCl_{RC\_mod}} = 1 - \frac{\left(C_{A_{out}}\right)_{cc}}{C_{A_{in}}} \tag{28}$$

where $C_{A_{in}}$ is the HCl concentration at the inlet of the RC and $\left(C_{A_{out}}\right)_{cc}$ is the HCl concentration at the exit of the cyclone concentrator, which is equal to the HCl concentration at the exit of the last CSTR (N_{cc}) for the cyclone concentrator.

Thus, when the reaction system is a system without recirculation, to calculate $\eta_{HCl_{RS\_mod}}$ the term $\left(C_{A_{out}}\right)_{cc}$ should be replaced by $\left(C_{A_{out}}\right)_{cr}$, and to calculate X_{RS_mod} the term corresponding to the cyclone concentrator $\left[\sum_{i=1}^{N_{cc}}(\dot{n}_{B_{rea}})_i\right]$ is null. The average particle collection efficiency in these systems (without recirculation) is, as expected, the average particle collection efficiency for the cyclone reactor $[(\eta_{capt.tot.})_{cr}]$.

Table 1
Model parameters.

Parameters	Symbol	Definition	Units
Reaction	k_s	Kinetic constant	m s^{-1}
	dif	Effective diffusion coefficient of A in D	m s^{-2}
	R_g	Initial radius of the grains	m
	$R_{c_{min.}}$	Minimum radius of the core in the grains	m
	M_B	Molar mass of B	kg kmol^{-1}
	ρ_B	Specific gravity of B	kg m^{-3}
	α	Ratio of the molar volumes of D to B	
Reactor	N_{cr}	Number of CSTRs in series in the cyclone reactor	
	N_{cc}	Number of CSTRs in series in the cyclone concentrator	
	f_{cap}	Solid fraction captured between CSTRs that is unavailable to continue to react	
	$f_{r_{sol.}}$	Recirculation solid fraction in ReCyclone systems	
	f_{rgas}	Recirculation gas fraction in ReCyclone systems	
	V_{cr}	Cyclone reactor volume	m^3
	V_{cc}	Cyclone concentrator volume	m^3
	$(\eta_{capt.tot.})_{cr}$	Average particle collection efficiency for the cyclone reactor	%
	$(\eta_{capt.tot.})_{RC}$	Average particle collection efficiency for the ReCyclone systems	%

2.3. Model parameters

The model incorporates several parameters that were classified as reaction parameters and reactor parameters. Table 1 presents the model parameters grouped according to the adopted classification.

Based on the characterization of the reaction systems tested and experimental results obtained some model parameters are known or can be calculated. The other parameters were estimated by optimization. A brief description of each parameter is presented next. When appropriate, the value or the calculus methodology is also given.

2.3.1. Reaction parameters

The reaction parameters usually referred to as kinetic parameters must be equal in all three reaction systems and independent of the system, because they are intrinsic parameters of the reaction that occurs and of the operating conditions used. In the absence of results to assign these parameters, when the reaction system is a cyclone, they were estimated by optimization. A range of 1.0×10^{-3} to 1.0×10^5 m s^{-1} was set for k_s, and 1.0×10^{-12} to 1.0×10^{-7} m^2 s^{-1} for dif. The wide ranges selected for these parameters is related to the variability of values found in the literature for the reaction process consisting of calcium compounds/HCl [9,15,24–29], depending on the system considered and the reaction conditions used.

The other reaction parameters when the reaction product is CaCl$_2$·2H$_2$O are shown in Table 2. The values of R_g and ρ_B were obtained in the characterization of solid reactant by Fonseca et al. [9] and the procedure of calculating $R_{c_{min.}}$ is given in Appendix A.

2.3.2. Reactor parameters
2.3.2.1. Number of CSTRs in series in the cyclone reactor.
In a preliminary approach it was found that the number of CSTRs in series in the cyclone reactor should have a distinct value for each reactor system, because the flow hydrodynamics is in principle different. The cyclone reactor used in the RC, although with the same geometry (Hurricane), has a different size. Not only the particles, collection

Table 2
Reaction system parameters.

Parameter	Value
R_g	1.5×10^{-7} m
$R_{c_{min.}}$	9.32×10^{-8} m
M_B	74.09 kg kmol^{-1}
ρ_B	2350 kg m^{-3}
α	2.37

efficiency is different, but also the gas average velocity at the inlet of the cyclone reactor (both the particles' collection efficiency and the average gas velocity are lower for the larger cyclone reactor, Hurricane 2.6). The modified Stairmand HE cyclone reactor must also have a different behavior than expected in Hurricane cyclones due not only to its different geometry, but also because it had a much larger average gas velocity at the inlet of the cyclone.

Accordingly, the model will incorporate the parameter N_{cr} associated with each cyclone reactor studied, i.e., $N_{cr\_RC\ 2}$ for the cyclone reactor of RC 2, $N_{cr\_RC\ 2.6}$ for the cyclone reactor of RC 2.6 and $N_{cr\_St\ HE}$ for the St HE. These three parameters are unknown and were determined by optimization.

2.3.2.2. Number of CSTRs in series in the cyclone concentrator.
The cyclone concentrator is a straight-through cyclone. Thus, the gas and solid flow in this cyclone may be well described considering it as a perfectly mixed reactor. However, in the absence of knowledge about the best reactor to describe the cyclone concentrator, it was considered that it is well described by a plug flow (the gas and the solid flows are described by CSTRs placed in series (N_{cc}), as found in the cyclone reactor except the fact that solid capture does not occur). As N_{cc} is an unknown model parameter, it was also determined by optimization.

2.3.2.3. Solid fraction captured between CSTRs that is unavailable to continue to react.
As previously mentioned, the flow hydrodynamics are different in each of the reaction systems studied and consequently also in their respective cyclone reactors. This phenomenon may influence either N_{cr} or $\eta_{f_{cap}}$ by the parameter f_{cap} [Eq. (7)]. Thus, f_{cap} may have different values depending on the cyclone reactor considered. So, the model also incorporates $f_{cap\_RC\ 2}$, $f_{cap\_RC\ 2.6}$ and $f_{cap\_St\ HE}$ as parameters to be obtained by optimization.

2.3.2.4. Recirculation gas and solid fraction in the ReCyclone systems.
The recirculation solid fraction $(f_{r_{sol.}})$ in the ReCyclone systems at laboratory scale is an unknown. However, for purposes of modeling this was considered equal to the recirculation gas fraction (f_{rgas})

Table 3
Useful volume in the reaction systems.

Reaction system	$V_{cr} \times 10^5$ (m^3)	$V_{cc} \times 10^5$ (m^3)
RC 2	1.06	2.86
RC 2.6	2.34	2.87
St HE	1.07	–

Table 4
Experimental conditions and selected results for the extraction of parameters by optimization.

Reaction system	$Q \times 10^4$ (N m^3 s^{-1})	$C_{A_{in}} \times 10^2$ (mol m^{-3})	$\dot{W}_{B_{in}} \times 10^7$ (kg s^{-1})	X_{RS} (%)	$\eta_{HCl_{RS}}$ (%)
RC 2		0.734–1.82	1.07–3.65	12.3–25.8	9.64–84.2
RC 2.6	2.9 ± 0.1	0.686–1.84	1.04–6.65	17.1–31.3	16.0–93.5
St HE		0.759–1.85	1.40–3.19	14.1–20.8	11.9–69.4

because the outlet of the Hurricane cyclone presents a very low content of solids, essentially consisting of very fine particles due to the high particle collection efficiency found in the Hurricane cyclone studied. For the recirculation gas fraction the value determined in the study developed by [30] was used. These authors conducted a

study at laboratory scale using a ReCyclone system similar to RC 2 tested in this work and obtained $f_{r_{gas}} \approx 14\%$ when the gas flow at the inlet of the RC was 2.9×10^{-4} N m^3 s^{-1}. For the RC 2.6 the recirculation gas and solid fraction should be slightly higher than in the RC 2 due the lower pressure drop in Hurricane 2.6. How-
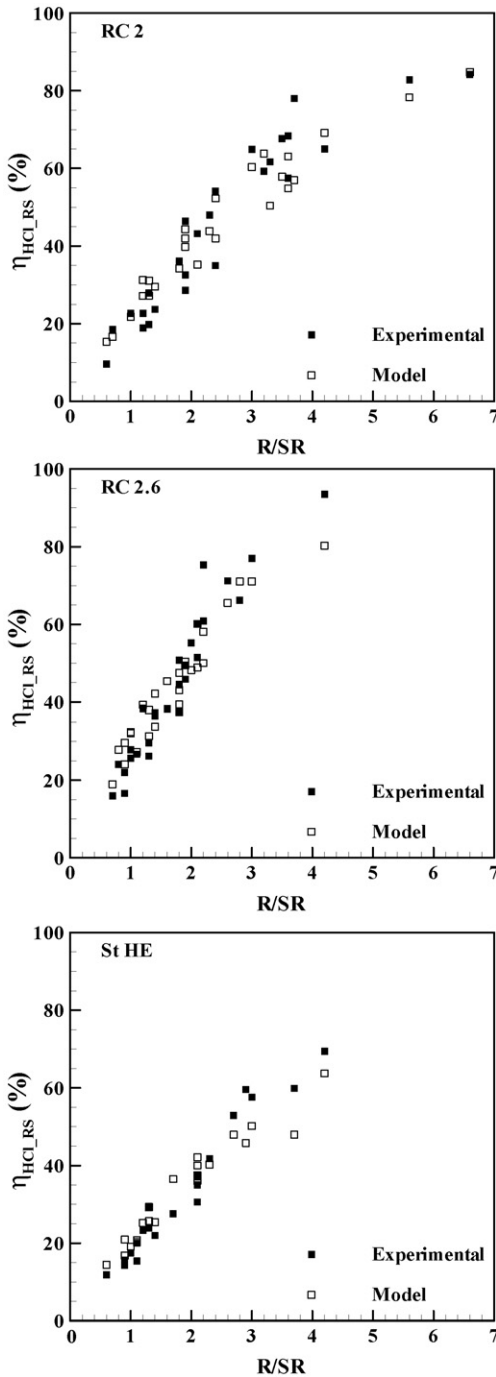
Fig. 2. Experimental results and predicted by the model for the HCl removal efficiency.
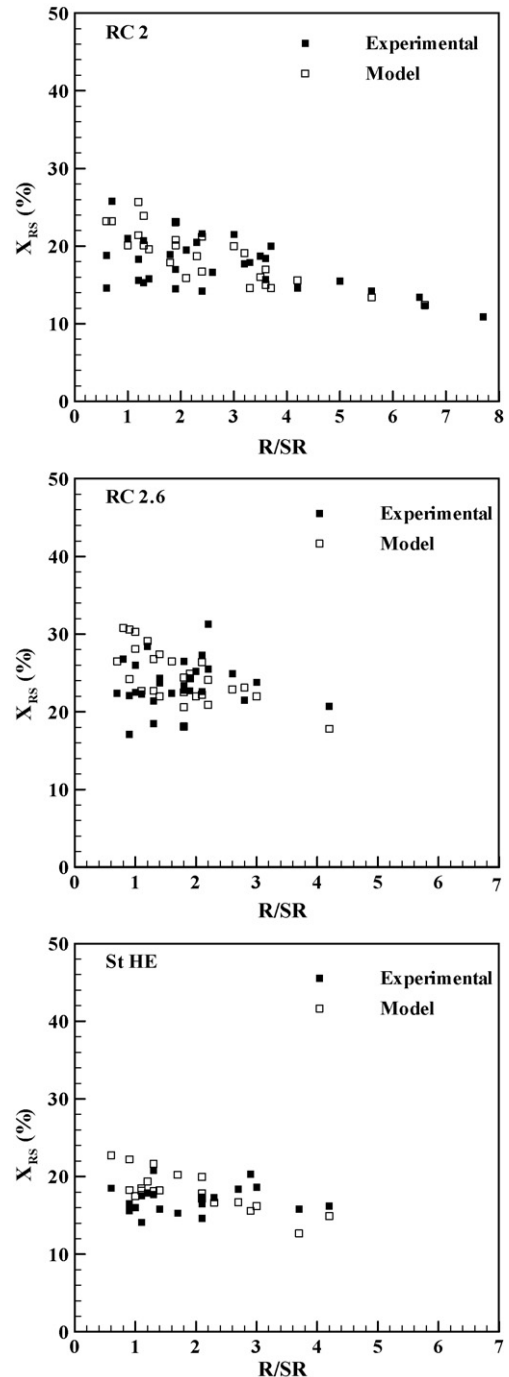
Fig. 3. Experimental results and predicted by the model for the solid reactant conversion.

ever, in the developed model, it was considered that both ($f_{r_{gas}}$ and $f_{r_{sol.}}$) are independent of the particular RC and take the value of 14%. The consideration that $f_{r_{gas}} = f_{r_{sol.}}$ means that the cyclone concentrator is operating as a flow divider and not as a concentrator. At laboratory scale for the Hurricane cyclones used, as well as from experimental evidence at pilot scale [31], this hypothesis is perfectly acceptable. This derives from the fact that the Hurricane cyclones are very efficient, letting only very fine particles escape collection. Thus, the recirculation flow has these fine particles, which are not greatly affected by the centrifugal forces present in the recirculation straight-through cyclone.

2.3.2.5. Cyclone reactor volume and cyclone concentrator volume.
The useful volumes for reaction in the cyclone reactor (V_{cr}) (Hurricane) and in the cyclone concentrator (V_{cc}) are shown in Table 3. The value of V_{cr} was calculated based on the work of Licht [32] and the subsequent correction made by Clift et al. [33].

2.3.2.6. Average particle collection efficiency in the reaction systems.
The reaction systems studied with recirculation (RC 2, RC 2.6) in the presence of reaction showed, with a confidence level of 95%, average particle collection efficiencies of (91.8 ± 0.6)% and (96.0 ± 0.3)% in the RC 2.6 and RC 2, respectively. For the reaction system without recirculation (St HE) this efficiency was (96.4 ± 0.5)%.

2.3.2.7. Average particle collection efficiency in the cyclone reactor.
The average particle collection efficiency in the cyclone reactors (Hurricane) that incorporate the ReCyclone systems in the presence

of reaction was (95.5 ± 0.4)% in the Hurricane 2 and (90.6 ± 0.6)% in the Hurricane 2.6, with a confidence level of 95%.

2.4. Extraction of the model parameters by optimization

According to the above mentioned, the 9 model parameters to be estimated by optimization are: k_s, dif, $N_{cr\_RC\ 2}$, $N_{cr\_RC\ 2.6}$, $N_{cr\_St\ HE}$, $f_{cap\_RC\ 2}$, $f_{cap\_RC\ 2.6}$, $f_{cap\_St\ HE}$ and N_{cc}.

For this non-linear optimization, the MSGA stochastic adaptive random search algorithm [34] was used. The objective function is the square sum of the difference between the experimental results and those predicted by this model, simultaneously for the acid removal efficiency ($\eta_{HCl_{RS}}$) and for the solid reactant conversion (X_{RS}). So, the objective function ($f_{obj.}$) to minimize is defined as:

$$f_{obj.} = \sum_{i=1}^{N_{exp.}} \left[\left(\eta_{HCl_{RS\_mod}} - \eta_{HCl_{RS}} \right)^2 + (X_{RS\_mod} - X_{RS})^2 \right] \quad (29)$$

where $N_{exp.}$ is the number of experimental data points. This optimization considers simultaneously all experimental trials conducted in the three reaction systems corresponding to the experimental conditions and results presented in Table 4.

Considering the large number of parameters to be obtained by optimization, a preliminary optimization was performed. A critical review of the results from this initial optimization found that the variables N_{cc} and N_{cr} progressed to the upper limit of their allowable range. Thus, these upper limits were relaxed and additional optimization runs were carried out.
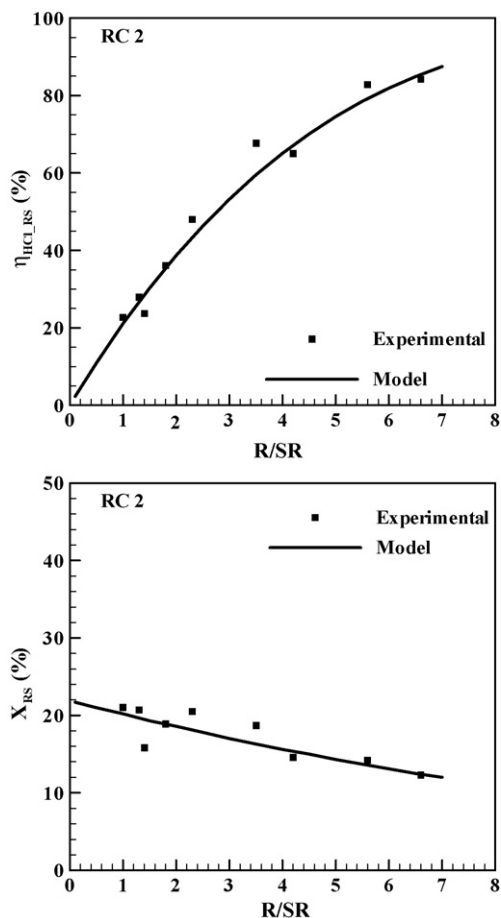

Fig. 4. Experimental results and predict by the model for RC 2 at $C_{A_{in}} = (1.03 \pm 0.050) \times 10^{-2}$ mol m^{-3}.
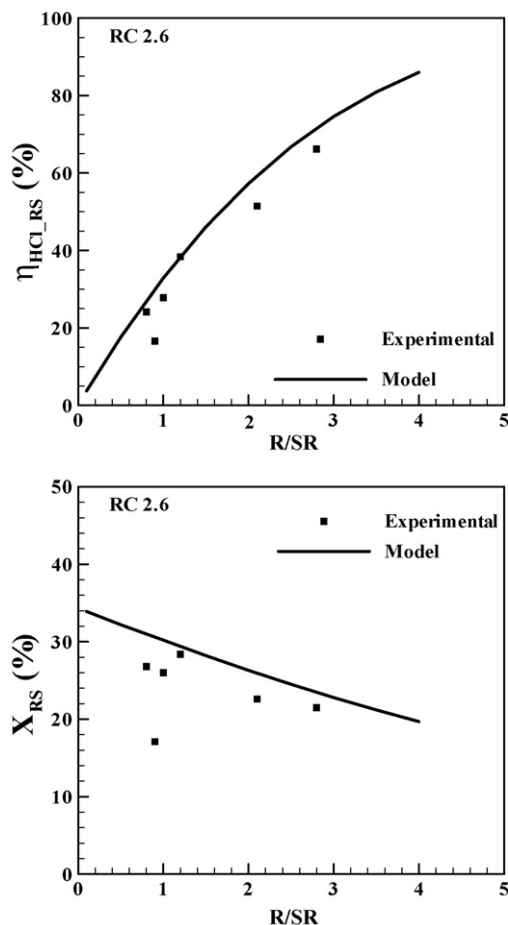

Fig. 5. Experimental results and predict by the model for RC 2.6 at $C_{A_{in}} = (1.78 \pm 0.050) \times 10^{-2}$ mol m^{-3}.

Table 5
Average values of the model parameters.

Parameter	Symbol		Value
Reaction	dif		$5.04 \times 10^{-8} \, \text{m}^2 \, \text{s}^{-1}$
	R_g		$1.5 \times 10^{-7} \, \text{m}$
	$R_{c_{min.}}$		$9.32 \times 10^{-8} \, \text{m}$
	M_B		$74.09 \, \text{kg} \, \text{kmol}^{-1}$
	ρ_B		$2350 \, \text{kg} \, \text{m}^{-3}$
	α		2.37
Reactor	N_{cr}		100
	N_{cc}		1
	$f_{cap\_RC\,2}$		0.46
	$f_{cap\_RC\,2.6}$		0.77
	$f_{cap\_St\,HE}$		0.83
	$f_{rgas} = f_{rsol.}$		0.14
	V_{cr}	(Hurricane 2)	$1.06 \times 10^{-5} \, \text{m}^3$
		(Hurricane 2.6)	$2.34 \times 10^{-5} \, \text{m}^3$
		(St HE)	$1.07 \times 10^{-5} \, \text{m}^3$
	V_{cc}	(RC 2)	$2.86 \times 10^{-5} \, \text{m}^3$
		(RC 2.6)	$2.87 \times 10^{-5} \, \text{m}^3$
	$(\eta_{capt.tot.})_{cr}$	(Hurricane 2)	95.5%
		(Hurricane 2.6)	90.6%
	$(\eta_{capt.tot.})_{RS}$	(RC 2)	96.0%
		(RC 2.6)	91.8%
		(St HE)	96.4%

For the reaction parameters (kinetics), it was observed that the parameter k_s systematically changed to the value assigned to its upper limit $(1 \times 10^5 \, \text{m} \, \text{s}^{-1})$ while dif remained at values of order of magnitude of $10^{-8} \, \text{m}^2 \, \text{s}^{-1}$. The calculation of the time constants associates with those kinetics parameters $\left(\tau_{k_s}\right)$ and (τ_{dif}), respectively $\tau_{k_s} = (R_g/k_s) \approx 1.5 \times 10^{-12} \, \text{s}$ and $\tau_{dif} = (R_g^2/dif) \approx 4.5 \times 10^{-7} \, \text{s}$, indicates that the inclusion of k_s in series with dif has no significant influence on the objective function value. Thus, the resistance associated with chemical reaction (k_s) was neglected. This hypothesis was validated by performing a new optimization considering only diffusion control, confirming that there were no significant changes either in f_{obj} or in the values found for the remaining parameters.

For the reactor parameters, it was observed that the value of N_{cr} systematically changed to a value close to the upper limit of its range of variation, taking values of the same order of magnitude in the different cyclone reactors tested. An opposite behavior was observed for the value of N_{cc} since it evolved always to the lower limit (one). Based on the values found for the objective function, practically invariant, we conclude that the model is not sensitive to these parameters. Given these results, further optimizations were realized to evaluate the hypothesis of $N_{cc} = 1$ and/or of N_{cr} being the same in the three cyclone reactors.

The optimization results show that considering $N_{cc} = 1$ and N_{cr} equal in the three cyclone reactors does not produce significant changes in the value of the objective function and hence in the model performance. However, it is important to note that the validation of the latter hypothesis allows reducing by half the number of model parameters obtained by optimization.

Finally, the hypothesis that considers the parameter f_{cap} equal for all reactors was also tested. The most relevant fact observed was
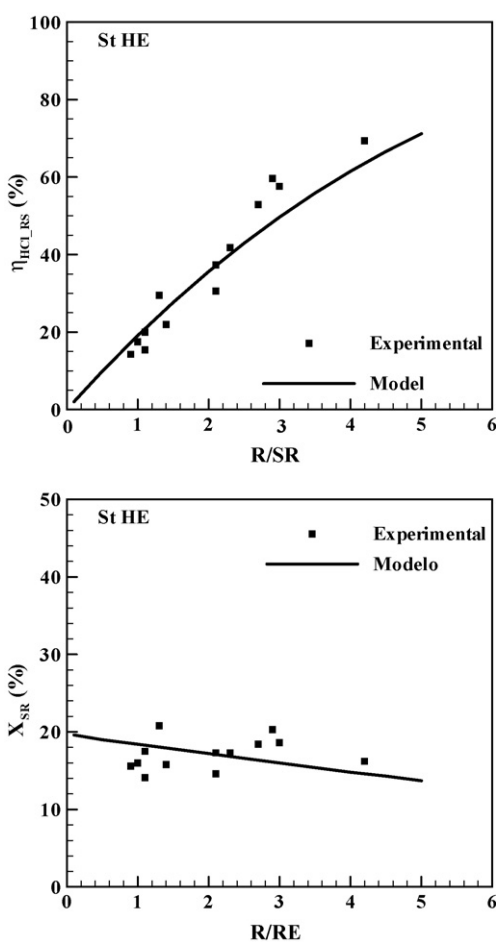

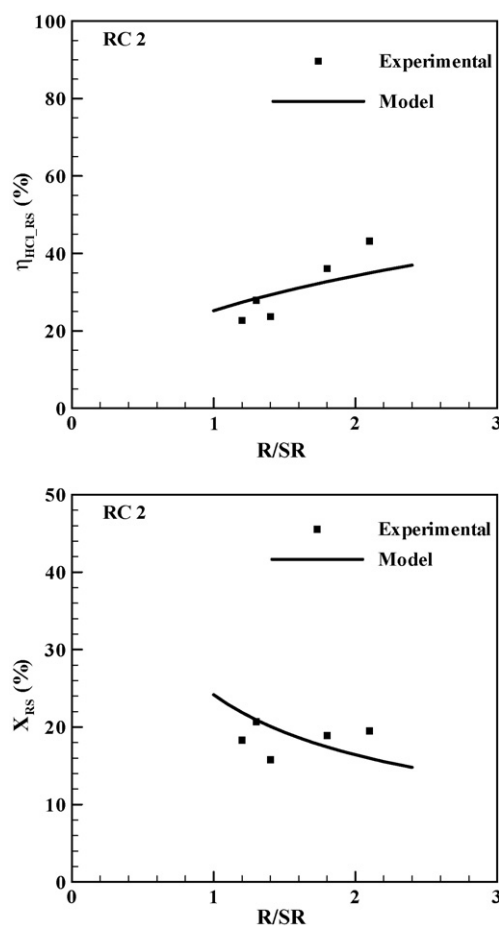**Fig. 6.** Experimental results and predict by the model for the St HE at $C_{A_{in}} = (1.23 \pm 0.037) \times 10^{-2} \, \text{mol} \, \text{m}^{-3}$.

Fig. 7. Experimental results and predict by the model for the RC 2 at $\dot{W}_{B_{in}} = (2.01 \pm 0.15) \times 10^{-7} \, \text{kg} \, \text{s}^{-1}$.

the increase in the value of the objective function, indicating that not only f_{cap} has an important role in the model, but it is intrinsic of each cyclone reactor.

From the analysis of the preliminary optimization results, it was concluded that:

- The control resistance is the diffusion of the gaseous reactant in the layer of solid product formed (dif);
- The cyclone reactor can be described by the same number of the CSTRs placed in series (N_{cr}) for the three cyclone reactors studied;
- The existing cyclone concentrator in RCs can be described by a Perfect Mixed Flow reactor ($N_{cc} = 1$);
- The solid fraction which is captured between CSTRs and that is unavailable for further reaction (f_{cap}) is dependent on the cyclone reactor.

Thus, the minimum number of model parameters that should be obtained by optimization was reduced from an initial nine down to four, one associated with the reaction parameters (dif) and the other intrinsic to each cyclone reactor ($f_{cap\_RC\ 2}, f_{cap\_RC\ 2.6}, f_{cap\_St\ HE}$).

It could also be concluded that dif is independent to N_{cr} if this parameter is greater than 5. For f_{cap} in each cyclone reactor it was found that this parameter is practically constant for values of N_{cr} above 50. Thus, with a value of $N_{cr} = 100$ selected, the other model parameters, obtained from 10 optimization runs (MSGA, being a stochastic algorithm, its results must be evaluated on a statistical basis) take the following final values (with a confidence level of 95%):

- $dif = (5.04 \pm 0.09) \times 10^{-8}$ m^2 s^{-1}
- $f_{cap\_RC\ 2} = 0.46 \pm 0.03, f_{cap\_RC\ 2.6} = 0.77 \pm 0.02, f_{cap\_St\ HE} = 0.83 \pm 0.02$

The small confidence intervals indicate a good precision in the optimization results. Since MSGA is a global search procedure, the results also indicate a good accuracy.

Table 5 presents a summary of all model parameters and their average values. As mentioned previously the model only considers the reaction phenomenon at grain level where the possible resistances were the chemical reaction (k_s) and the diffusion of the gaseous reactant in the layer of solid product formed (dif). Hence the resistance to diffusion of HCl in the solid reactant pores (def) was neglected. However, for the temperature of reaction of 53 °C, the variation that occurs in that diffusion coefficient based on the 'Dusty Gas Model' results in an initial estimate (i.e., before reaction) of $def = 3.3 \times 10^{-6}$ m^2 s^{-1}, that decreases after the reaction to an estimate of around 1.3×10^{-6} m^2 s^{-1}, based on the experimental results, or of 1.7×10^{-6} m^2 s^{-1} using the model predictions.

Making a comparison between the values obtained for def and dif we conclude that the hypothesis of considering non-significant the resistance to diffusion of HCl in the solid reactant pores is acceptable.

2.5. Model validation

To validate the model, a comparison was carried out between the results predicted by the model and those obtained experi-
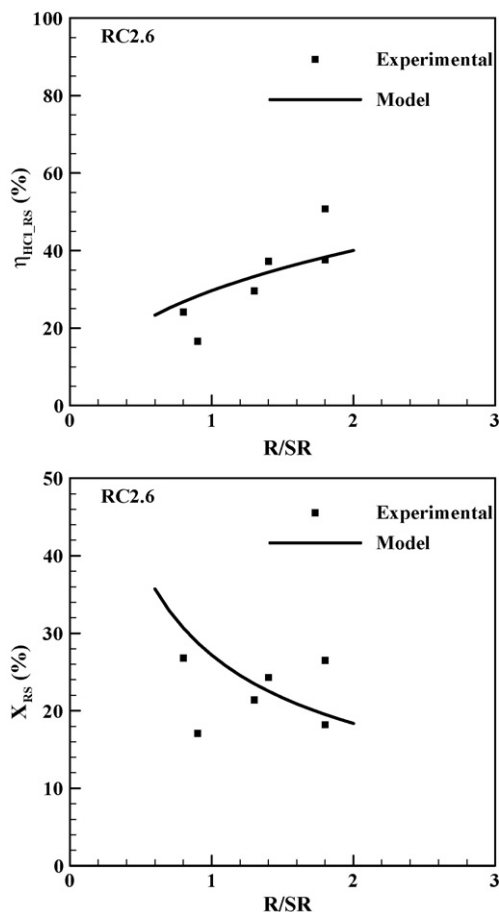

Fig. 8. Experimental results and predict by the model for the RC 2.6 at $\dot{W}_{B_{in}} = (1.81 \pm 0.20) \times 10^{-7}$ kg s^{-1}.

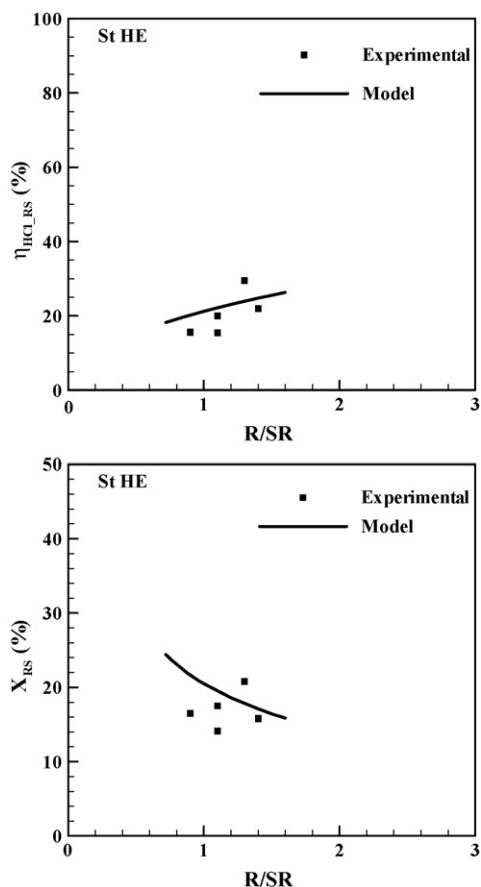Fig. 9. Experimental results and predict by the model for the St HE at $\dot{W}_{B_{in}} = (2.01 \pm 0.31) \times 10^{-7}$ kg s^{-1}.

mentally for the HCl removal efficiency $\left(\eta_{\text{HCl}_{RS}}\right)$ and for the solid reactant conversion (X_{RS}), as long as the experimental conditions presented in Table 4 are verified.

The experimental results and those predicted by the model for every R/SR, for both $\eta_{\text{HCl}_{RS}}$ and X_{RS} are illustrated in Figs. 2 and 3, respectively.

Comparison between the experimental results and those predicted by the model for the HCl removal efficiency (Fig. 2) and for the solid reactant conversion (Fig. 3) indicate that the proposed model describes well the experimental observations.

The ratio R/SR reflects the relationship between the mass flow rate of solid reactant $\left(\dot{W}_{B_{in}}\right)$ and the HCl concentration $\left(C_{A_{in}}\right)$ fed to the reaction system at any time (R) and the stoichiometric ratio of these two experimental variables (SR). Since these experimental variables are independent, we selected a fixed HCl concentration $\left(C_{A_{in}}\right)$ and a fixed mass flow rate of solid reactant $\left(\dot{W}_{B_{in}}\right)$ in each reaction system to support the model predictions. Each range was selected to include the largest number of experimental data points within a small variation ($\pm 10\%$), both for the HCl concentration and the mass flow rate of solid reactant.

Figs. 4–9 present the experimental results and those predicted by the model for a constant HCl concentration (Figs. 4–6) and for a constant mass flow of solid reactant (Figs. 7–9) at the inlet of the three reaction systems.

Analyzing the results illustrated in Figs. 4–9 and taking into account the variability of the experimental data, it can be concluded that the model predicts with reasonable accuracy the behavior observed experimentally in any of the reaction systems. A similar

behavior was found for other values of the experimental variables, within the experimentally range studied.

A comparative study was also done using the model, considering the three reaction systems at a fixed HCl concentration at the inlet of the reaction system for different values of $\dot{W}_{B_{in}}$ (translated into the ratio R/SR).

In Fig. 10 it is clear that the model predicts a higher reaction behavior for ReCyclone systems (RC 2 and RC 2.6) than the modified Stairmand HE cyclone (St HE). For ReCyclone systems, it appears that the reaction system that incorporates the largest cyclone reactor (Hurricane 2.6) shows superior reaction characteristics.

2.6. Model predictions for different operating conditions

Using the model, a study was carried out on the influence of some of the operating conditions in the reaction behavior for ReCyclone systems. Given the reaction superiority verified in RC 2.6 this system was selected.

Thus, the influence of the variation of the initial grain size (R_g) and the operating variables at the inlet of the reaction system (HCl concentration and mass flow rate of solid reactant), namely in the HCl removal efficiency $\left(\eta_{\text{HCl}_{RS\_mod}}\right)$ and in the solid reactant conversion (X_{RS_mod}), was studied.

2.6.1. Initial radius of the grains

In the study of the influence of the initial radius of the grains (R_g) this parameter was varied between 1.5×10^{-6} and 1.0×10^{-7} m (interval allowed by the model for this parameter) and the operating variables had the following values: $C_{A_{in}} = 1.35 \times 10^{-2}$ mol m^{-3};
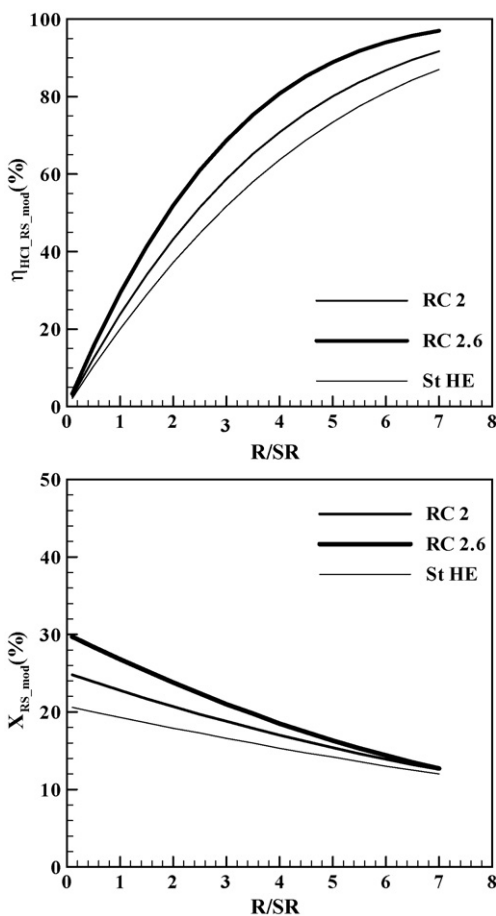

Fig. 10. Comparison between the reaction systems based on the model predictions at $C_{A_{in}} = 1.35 \times 10^{-2}$ mol m^{-3}.
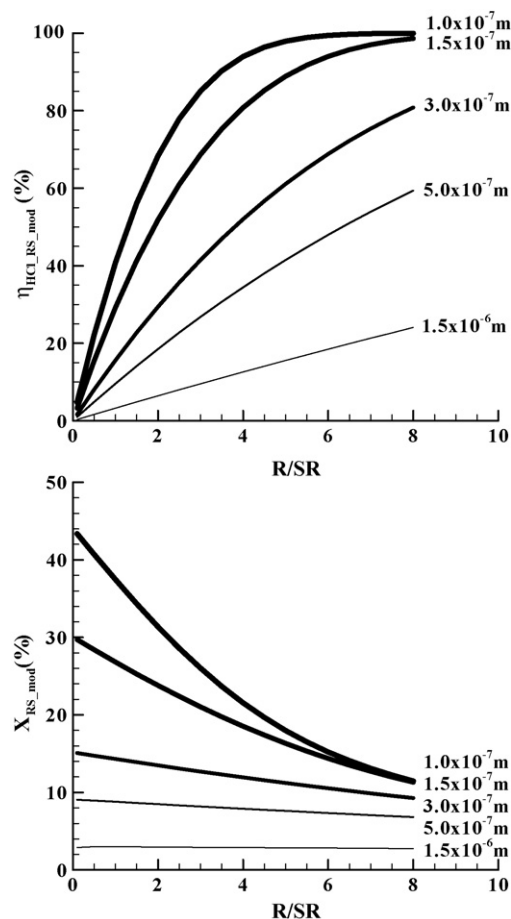

Fig. 11. Model predictions for different values of R_g for RC 2.6.

$Q = 2.9 \times 10^{-4}$ N m^3 s^{-1} and $\dot{W}_{B_{in}}$ varied between 1.75×10^{-8} and 1.40×10^{-6} kg s^{-1} (in order to have a variation of R/SR between 0.1 and 8). Fig. 11 illustrates the model predictions for $\eta_{HCl_{RS\_mod}}$ and for X_{RS_mod} in the reaction system RC 2.6.

The results presented in Fig. 11 show that the reaction is favored with by decreasing the radius of the reacting grain. It is noted that for values of $R_g = 1.5 \times 10^{-6}$ m (upper limit of the interval allowed by the model) the maximum HCl removal efficiency is 24% for $R/SR = 8$ and $X_{RS\_mod} \approx 3\%$ regardless of the value R/SR.

2.6.2. HCl concentration and mass flow rate of solid reactant, at the inlet of the reaction system

Considering the range allowed for $C_{A_{in}}$ by the model (between 5.0×10^{-5} and 4.0×10^{-2} mol m^{-3}) and for $W_{B_{in}}$ (between 1.00×10^{-8} and 9.00×10^{-7} kg s^{-1}) and keeping $Q = 2.9 \times 10^{-4}$ N m^3 s^{-1}, the influence of the two experimental variables ($C_{A_{in}}$ and $\dot{W}_{B_{in}}$) in the reaction behavior of RC 2.6 to a maximum $R/SR = 8$ was studied. Results for $\eta_{HCl_{RS\_mod}}$ and X_{RS_mod} according to R/SR are illustrated in Figs. 12 and 13, respectively.

For a fixed HCl concentration at the inlet of the reaction system, the model predicts an increase in the HCl removal efficiency with the increase in R/SR (Fig. 12). A similar behavior was obtained, as expected, for a fixed mass flow rate of solid reactant at the inlet of the system (Fig. 13). For the solid reactant conversion there is an opposite behavior, i.e., X_{RS} increases with the decrease of R/SR either for a fixed HCl concentration (Fig. 12) or for a fixed mass flow rate of solid reactant (Fig. 13).

As verified experimentally, the dry-cleaning of gaseous emissions containing HCl with solid particles of Ca(OH)$_2$ is more efficient at higher R/SR ratios.
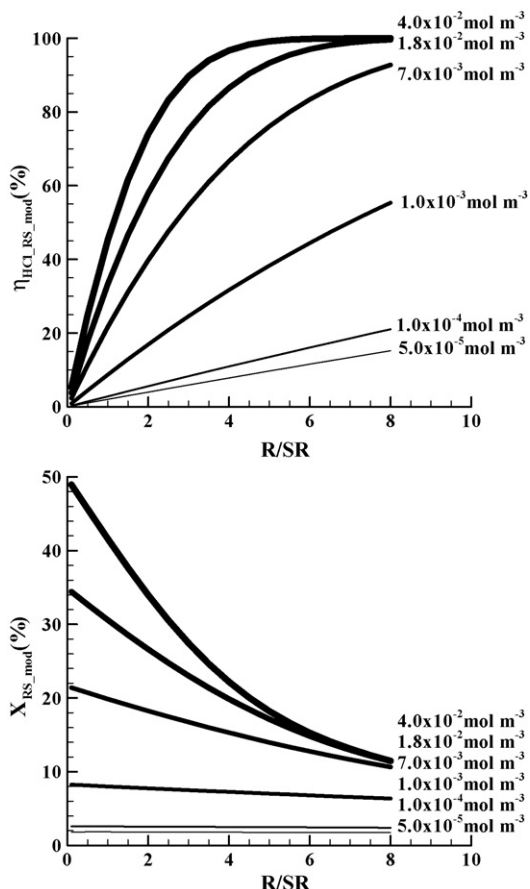

Fig. 12. Model predictions for different values of $C_{A_{in}}$ for RC 2.6.
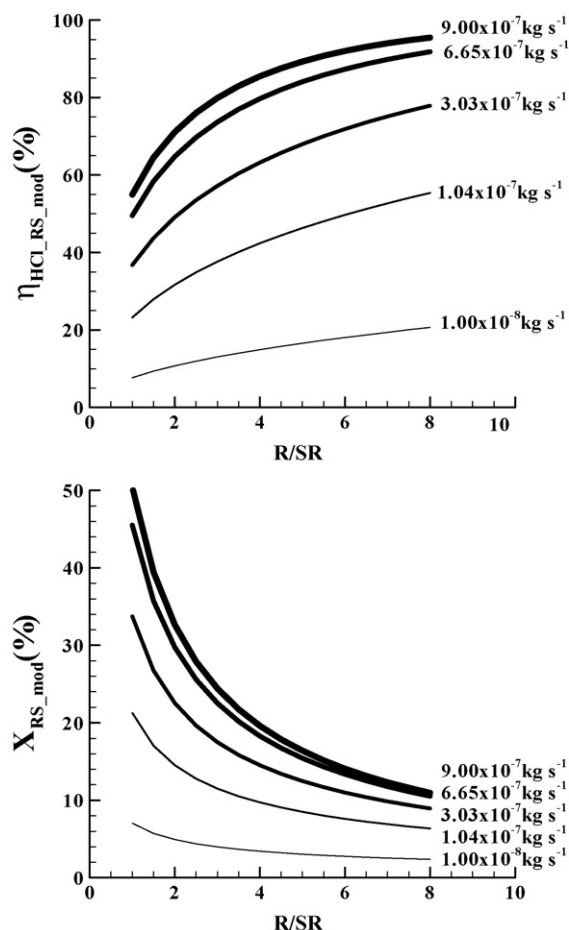

Fig. 13. Model predictions for different values of $\dot{W}_{B_{in}}$ for RC 2.6.

3. Conclusions

For the modeling of the dry-cleaning of HCl with hydrated lime in reaction systems composed either by a single reverse-flow cyclone (Hurricane) or by a series of cyclone/concentrator (ReCyclone systems), the Modified Grain Model was selected to describe the behavior of the reaction process. The hydrodynamics in the cyclone reactors were described as plug flow, approximated by N CSTRs placed in series, both for the solid and gaseous phases. The developed model considered only the reaction phenomenon at grain level with the possible resistances of chemical reaction (k_s) and diffusion of the gaseous reactant in the layer of solid product formed (dif). The resistance to diffusion of HCl in the solid reactant pores (def) was neglected but the validity of this hypothesis was subsequently confirmed.

The model incorporates several parameters. Some of those (dif, k_s, f_{cap}, N_{cr} and N_{cc}) were estimated by optimization taking into account the experimental results obtained. From preliminary optimization results, it was found that the resistance associated with the chemical reaction (k_s) could be neglected as compared to the resistance associated with the effective diffusion of gaseous reactant in the layer of solid product formed (dif). This conclusion was taken based on the values obtained for τ_{k_s} ($\approx 1.5 \times 10^{-12}$ s) and for τ_{dif} ($\approx 4.5 \times 10^{-7}$ s), when $k_s = 10^5$ m s^{-1} and $dif \approx 5 \times 10^{-8}$ m^2 s^{-1}.

The values obtained for these two parameters (k_s and dif) usually referred to as kinetic parameters, are within the range of values found in the literature for the reaction process under study. Intrinsic parameters for the reactor, which were obtained by optimization, were $N_{cc} = 1$ and when $N_{cr} > 50$,

with the values obtained for f_{cap} and dif independent of N_{cr}. Finally, $N_{cr} = 100$ was fixed for the final optimization, giving the estimated values for the other model parameters as follows: $dif = (5.04 \pm 0.09) \times 10^{-8}\ m^2\ s^{-1}$, $f_{cap\_RC2} = 0.46 \pm 0.03$, $f_{cap\_RC2.6} = 0.77 \pm 0.02$ and $f_{cap\_St\,HE} = 0.83 \pm 0.02$.

A good agreement was found between the experimental results and those predicted by the model, where the control resistance is the diffusivity of the acid in the layer of solid product formed.

The model was used to study the effect of varying some operating conditions (initial grain size, HCl concentration and mass flow rate of solid reactant) on the HCl removal efficiency and solid reactant conversion. It was found that the process of dry-cleaning of gaseous emissions containing HCl with solid particles of $Ca(OH)_2$, is much more efficient (in terms of acid removal and solid reactant conversion) for smaller initial grain size and for the larger ReCyclone system. Also, ReCyclone systems are more efficient as dry gas cleaning devices than single reverse-flow cyclone reactors.

For a fixed HCl concentration or mass flow rate of solid reactant at the inlet of the reaction system, the model predicts an increase in the HCl removal efficiency with the increase in R/SR. The opposite occurs for the solid reactant conversion.

As future work, it is important to consider the effect of the size distribution of particles of the solid reactant, the reaction phenomenon not only at the grain level but also at particle level, and the variation of effective diffusion coefficient of gas in the layer of solid product in the course of the reaction. These improvements will allow a more realistic application of the model to cases where there is a high solid reactant conversion, a wide size distribution of reactant, or to cases where the resistance associated with diffusion of gas in the particles pores may be relevant.

Acknowledgements

Appendix A. Determination of the minimum radius of the unreacted core in the grain

The radius of the unreacted core in the grains will be minimal $\left(R_{c_{mín.}}\right)$ when the maximum conversion of solid reactant (X_{max}) is achieved and they are related by the following expression:

$$R_{c_{mín.}} = R_g(1 - X_{max})^{1/3} \tag{A.1}$$

The solid reactant can be described by porous particles that consist in clusters of non-porous grains. When the molar volume of solid product formed is higher than that of the solid reactant, a critical value for the initial porosity of the solid reactant is pre-defined, which determines if the total conversion of solid reactant can be attained. If the initial porosity of the solid reactant is less than this critical value, the pores of the solid reactant block before complete conversion of the solid reactant [2].

The critical value for the initial porosity is given by the ratio $(\alpha - 1)/\alpha$, where α is the ratio of the molar volumes of the solid product formed to the solid reactant [2].

For the reaction under study, when the solid product formed is $CaCl_2 \cdot 2H_2O$, the critical value of the solid reactant initial porosity is 0.58 [36] since $\alpha = 2.37$ [9,22]. As the $Ca(OH)_2$ employed for this work presents an initial porosity $\left(\varepsilon_{s_0}\right)$ of 0.51, the total solid reactant conversion can never be complete.

Considering that the variation in the solid reactant porosity during the reaction (ε_s) may be related to the conversion (X) by [9]:

$$\varepsilon_s = \varepsilon_{s_0} - (1 - \varepsilon_{s_0})(\alpha - 1)X \tag{A.2}$$

and taking into account that the solid reactant conversion is related to the initial radius of the grains (R_g) and radius of the unreacted core in the grains (R_c) in the following way [2,10,13,14]:

$$X = 1 - \left(\frac{R_c}{R_g}\right)^3 \tag{A.3}$$

The maximum solid reactant conversion achieved will have to correspond to $\varepsilon_s = 0$ and is given by:

$$X_{max} = \frac{\varepsilon_{s_0} - \varepsilon_s}{\left(1 - \varepsilon_{s_0}\right)(\alpha - 1)} \tag{A.4}$$

Eq. (A.4) shows that the value of $X_{max} = 76\%$ obtained for the selected solid reactant would correspond to a non-porous solid.

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