Latin American Applied Research 34:111-118 (2004)

GAS-SOLID NON CATALYTIC REACTIONS: A MATHEMATICAL MODEL BASED ON HEAT TRANSFER ANALYSIS

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***Abstract*— The analysis of temperature profiles in spherical samples under chemical reaction is presented here as an adequate tool to identify if a gas-solid reaction system belongs to the unreacted core model or to the progressive conversion one. This analysis has been applied to the thermal decomposition of natural carbonates (dolostone, limestone and travertine from San Juan, Argentina and limestone from Neuquén, Argentina). The mathematical model based on heat transfer combined with chemical reaction presented here, allows to predict temperature profiles in spherical samples of natural carbonates under thermal decomposition. Reaction times obtained from thermogravimetric studies of thermal decomposition of dolostones, and those predicted by the calculation procedure presented here, disagree in less than 12%.**

***Keywords*: Mathematical Modeling; Transport Processes; Heat Transfer; Kinetics; Reaction Engineering.**

I. INTRODUCTION

The study of an heterogeneous solid–gas reaction system usually involves heat and mass transport, and reaction kinetics, in order to predict its evolution under the chemical reactor operating conditions. Doraiswamy and Sharma (1984) presented a summary of mathematical models for heterogeneous gas-solid non-catalyzed chemical reactions, which include parameters characterizing mass and energy transport, and the chemical reaction rate.

There are many works on mathematical modeling of gas-solid non-catalyzed reactions, having a wide range of mathematical complexity. Some of them are developed without application to a particular reaction system, that is, the authors assume the reaction kinetics, and the mass and heat transfer coefficients values (Seggiani *et al.*, 2000; Uhde and Hoffmann, 1997; Fatehi and Kaviany, 1997; Villa *et al.*, 1992; Villa and Quiroga, 1990). In other works, the results predicted by the models are compared with experimental data obtained for a particular reaction system, whose reaction kinetics, and mass and energy transport coefficients are known (Patisson *et al.*, 1998; Mutasher *et al.*, 1989; Bowen *et al*, 1989; Ulkutan *et al.*, 1982, Narsimhan, 1961).

In addition to mathematical complexity, another important feature to be considered is the calculation of the above mentioned parameters. An incorrect prediction can result in wrong conclusions when these models are used to describe real systems. We agree with Levenspiel opinion (1987) that "It is of little use to select a model which very closely mirrors reality but which is so complicated that we cannot do anything with it. Unfortunately, this all too often happens". Due to this, it seems advisable to use simple models, with a minimum of those parameters, when they are going to be applied to engineering problems.

The rate of some gas-solid non-catalyzed chemical reactions can be followed analyzing the structural changes that take place in the solid during the reaction. One of the properties that can show these changes is the diffusivity of reactants and products through the solid structure, although it is very difficult, and almost impossible, to measure variations in the diffusion rate of chemical species through the porous structure.

The use of properties characterizing heat transport in porous solids (e.g. effective thermal conductivity) to follow chemical reactions has some advantages over those describing mass transfer. For example, the determination of the thermal conductivity of a solid requires relatively simple experimental equipment, compared with that necessary to determine the effective diffusivity.

This work proposes an experimental method to determine if a gas-solid reaction system belongs to the unreacted core model or to the progressive conversion one, based in the measurement of temperature gradients between two isothermal surfaces, when heat flows constantly through a spherical sample. The analysis of the temperature profile, and its variations with time, allows to identify the material located between two isothermal surfaces, provided that the thermal conductivity of solid reactants and products is known. To detect changes in the temperature profile, the thermal conductivity of the solid reactant has to be different from that of the solid product.

Two calculation procedures, based on heat transfer combined with the chemical reaction, are developed to

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predict the reaction time as a function of the fractional conversion, one for a reaction belonging to the unreacted core model, the other for a reaction system corresponding to the progressive conversion model. These procedures are simpler than others proposed for similar systems (Muthaser *et al*., 1989; Ulkutan *et al*., 1982; Ishida and Wen, 1968).

The proposed procedures were applied to the thermal decomposition of dolostones from San Juan (Argentina). The chemical reaction rate was obtained from studies carried out previously in a thermogravimetric equipment described in detail in a former paper (Silva *et al*., 1999). The thermal conductivities of the solid reactant and product were determined experimentally (Silva *et al*., 2000). The reaction time predicted by the proposed procedure was compared with the one obtained from kinetic studies.

II. HEAT TRANSFER IN SOLIDS

The differential rate of heat flow between the gas surrounding the sample and the solid surface is:

$$dQ = h(T_g - T_0)dA_s \tag{1}$$

where:

dQ : Differential rate of heat flow
h : Global heat transfer coefficient
T_g : Temperature of the gas surrounding the sample
T_0 : Temperature of the solid surface
dA_s: Differential area of the solid

If the experiment is carried out with a spherical sample (radius R_0), and under radial symmetrical energy transfer conditions, (T_g-T_0) is constant for all points of the solid surface, then, in this case, the heat flow is:

$$Q = 4\pi R_0^2 h(T_g - T_0) \tag{2}$$

Depending on the temperature level, heat transfer between the gas and the solid takes place by different mechanisms. In each case, the global heat transfer coefficient between the gas and the solid surface has to be calculated.

When heat transfer between gas and solid takes place mainly by convection and radiation, Q can be calculated by:

$$Q = 4\pi R_0^2 \left[h_c\left(T_g - T_0\right) + \sigma\varepsilon\left(T_g^4 - T_0^4\right)\right] \tag{3}$$

where:

h_c: Heat transfer coefficient by convection
σ: Stefan-Boltzmann constant
ε: Emissivity

At about 623 K, heat transfer is carried out mainly by convection. In this regime, and under radial symmetrical thermal conditions:

$$Q = 4\pi R^2 h_c\left(T_g - T_0\right) \tag{4}$$

At about 900 K, the temperature at which some chemical reactions take place at a reasonable rate (e.g. thermal decomposition of carbonates), heat transfer is carried out mainly by radiation. In these cases, the heat flow can be calculated from a simplified form of Eq. (3):

$$Q = 4\pi R_0^2\left[\sigma\varepsilon\left(T_g^4 - T_0^4\right)\right] \tag{5}$$

When heat passes through the solid (without generation or absorption of energy, due to a chemical reaction) at a constant heat rate (Q), the equation relating the temperature (T) of an interior point (radius R) with that of the solid surface (T_0) of a spherical solid sample (Narsimhan, 1961), is:

$$Q = \frac{4\pi R R_0 k_e\left(T_0 - T\right)}{\left(R_0 - R\right)} \tag{6}$$

where:

R_0: Sample radius
k_e: Effective thermal conductivity of the solid

From Eq. (6), the temperature difference (ΔT), corresponding to two spherical surfaces can be determined, provided that the thermal conductivity of the material limited by those surfaces is known.

When no changes in the physical structure of the solid occur, the temperature difference ΔT, obtained applying Eq. (6) remains constant, although both temperatures may change.

When the solid is under chemical reaction, the thermal conductivity of the material can change substantially, mainly due to structural changes in it, and, due to this, variations in temperature profiles can be expected. The temperature profiles, and their variations with time, allow to know how the chemical reaction is taking place.

III. MATHEMATICAL MODEL BASED ON HEAT TRANSFER

When a gas-solid non-catalyzed chemical reaction takes place, mass and energy transport and reaction kinetics have to be combined.

Temperature and concentration profiles in the solid depend on mass transport rate, energy transport rate and absorption or evolution of heat due to the chemical reaction, which normally takes place at different rates in different points of the sample.

The mathematical model basically proposes to divide the sample into spherical shells (thickness $\Delta R = R_{j-1} - R_j$) and to carry out an energy balance in one of them [Eq. (7)]. The heat entering the "*j*" shell per unit of time (Q_{j-1}) is equal to the energy per unit of time necessary to carry out the chemical reaction (Q_{Rj}), plus the heat leaving the shell per unit of time (Q_j).

$$Q_{j-1} = Q_j + Q_{Rj} \tag{7}$$

$$Q_j = R_{j-1} R_j k_e\left(T_{j-1} - T_j\right) / (R_{j-1} - R_j) \tag{8}$$

$$Q_{Rj} = (4/3)\pi(\Delta H_r) r_{Qj} \left(R_{j-1}{}^3 - R_j{}^3\right) \qquad (9)$$

where:

ΔH_R: Heat of reaction

r_Q : Chemical reaction rate

Considering the heat transfer process, two different cases will be analyzed:

a) When heat entering one shell is totally consumed by the chemical reaction, no heat is transmitted to the following shell (Q_j=0) until the whole material of the shell has reacted completely. In this case the chemical reaction belongs to the unreacted core model.

The proposed mathematical model predicts that the temperature of the unreacted core will homogenize while the chemical reaction is taking place.

The conversion corresponding to the totally reacted "j" shell is calculated from the following equation:

$$X_j = \frac{(4/3)\pi(R_{j-1}^3 - R_j^3)}{(4/3)\pi R_0^3} = \frac{R_{j-1}^3 - R_j^3}{R_0^3} \qquad (10)$$

The time necessary to carry out the chemical reaction in each shell can be determined provided that the rate of the chemical reaction (r_{Qj}) is known.

These data should include the variation of the reaction time with conversion, temperature, and particle size, which are the operation variables taken into account when a chemical reactor is designed.

The following calculation program, whose logic diagram is shown in Fig. 1, allows predicting the radius of the unreacted core, and the temperature profile in terms of time.

Step 1

- The sample radius (R_0) is divided into N spherical shells (thickness $\Delta R = R_0/N$).

- Q_0 is calculated starting from Eq. (3), (4) or (5), depending on the temperature of the reaction.

- The conversion corresponding to the external shell (j=1) is calculated from Eq. (10)

The time necessary for the total conversion of the material of the external shell (Δt_1) is obtained from r_{Q1}, provided that $Q_0 = Q_{R1}$

For this step the model predicts that $T_1 = T_2 = \ldots. = T_N$

Step 2

- The temperature difference in the first shell ($T_0 - T_1$) is calculated from Eq. (6), using the thermal conductivity of the completely converted material. Q_0 has the value calculated in Step 1.

- The conversion corresponding to the following shell (j=2) is calculated from Eq. (10).

- The time necessary for the total conversion of the material of the second shell (Δt_2) is obtained from r_{Q2} provided that $Q_0 = Q_{R2}$.

- The total time of reaction is: $t = \sum_{i=1}^{2} \Delta t_i$ (11)

- The total conversion corresponding to t_i is:

$$X_{i,j} = \sum_{j=1}^{2} X_j \qquad (12)$$

- For this step the model predicts that $T_2 = T_3 = \ldots. = T_N$

Calculations detailed in Step 2 are repeated for the following shell until the last one is totally converted. This allows predicting the variation of the temperature profile with time.

b) When heat entering a shell is not totally consumed by the chemical reaction, heat flows to the following one. This happens in all shells, then, the energy balance [Eq. (7)] can be used to predict the temperature profile in terms of time.

The sequence of calculation, shown in Fig. 2, basically is:

- Partition of the total time of calculation into M intervals, $\Delta t = t/M$

- Selection of the number of shells (N), thickness $\Delta R = R_0/N$, in which the sample is going to be divided.

- Evaluation of Q_0, starting from Eq. (3), (4) or (5).

- The conversion corresponding to the totally reacted external shell (j=1), $X_{max}(j)$, is calculated from Eq. (10)

- The conversion reached in the first time interval (i=1), Δt (i), corresponding to the external shell (j=1), X (i,j), is calculated from r_Q, at temperature of the solid surface T_0

- The heat consumed by the chemical reaction in the external shell at the first interval of time Q_R (1,1) is calculated from ΔH_R and X (1,1)

- Q (1,1) calculation from Eq. (7)

- T (1,1) calculation, from Eq. (6)

- The calculation continues until the N shells have been considered (j = N) for the first Δt or until total conversion is reached, then it is repeated for the following Δt, and so on, until the total time of study is reached, or until total conversion reached is 1.

IV. VALIDATION OF THE PROPOSED CALCULATION PROCEDURE

In order to analyze the validity of the proposed calculation procedure, the thermal decomposition of natural carbonates of different origin and composition (limestone, dolostone and travertine from San Juan,

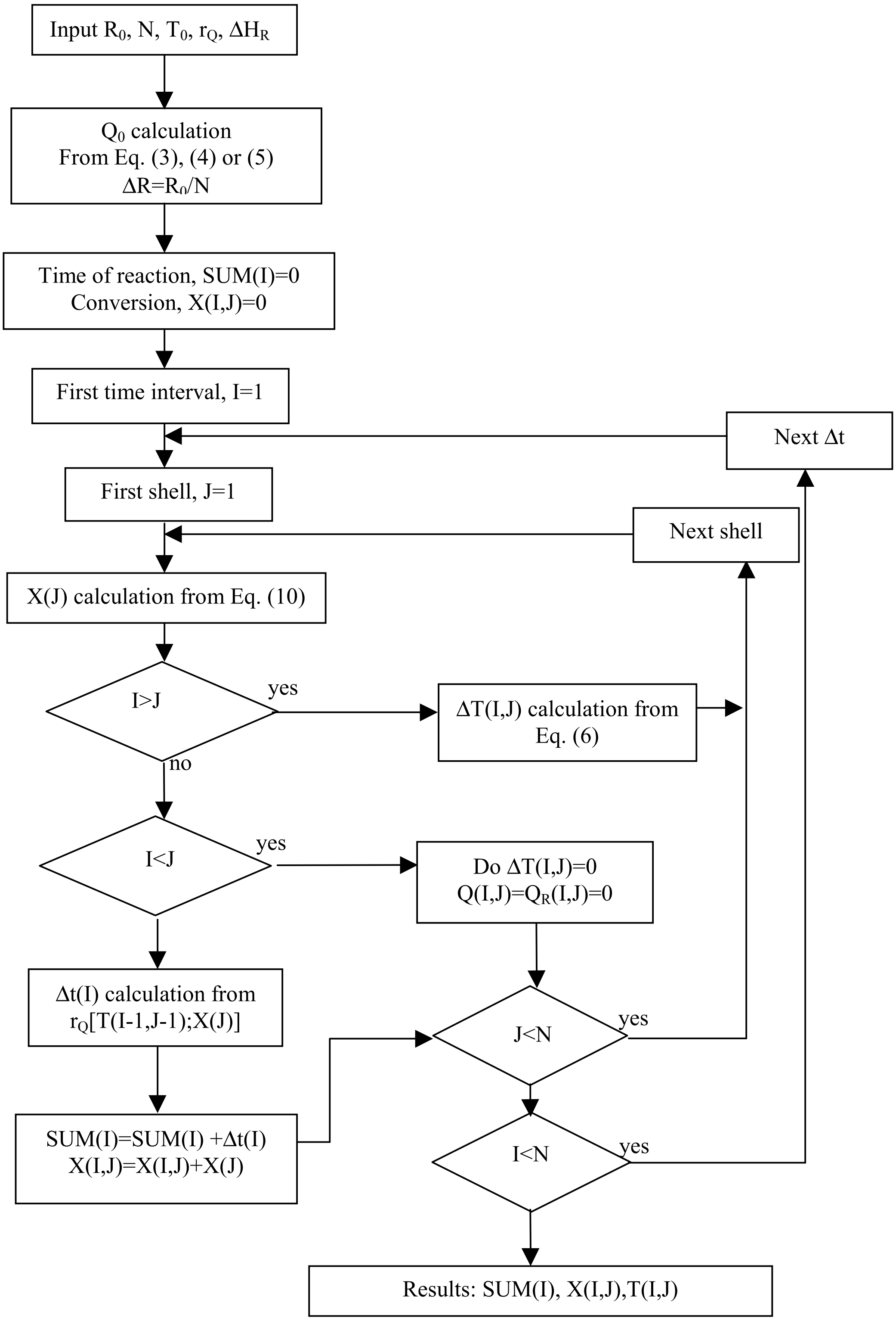

Fig. 1– Calculation flow chart for a gas-solid non catalytic reaction belonging to the unreacted core model.

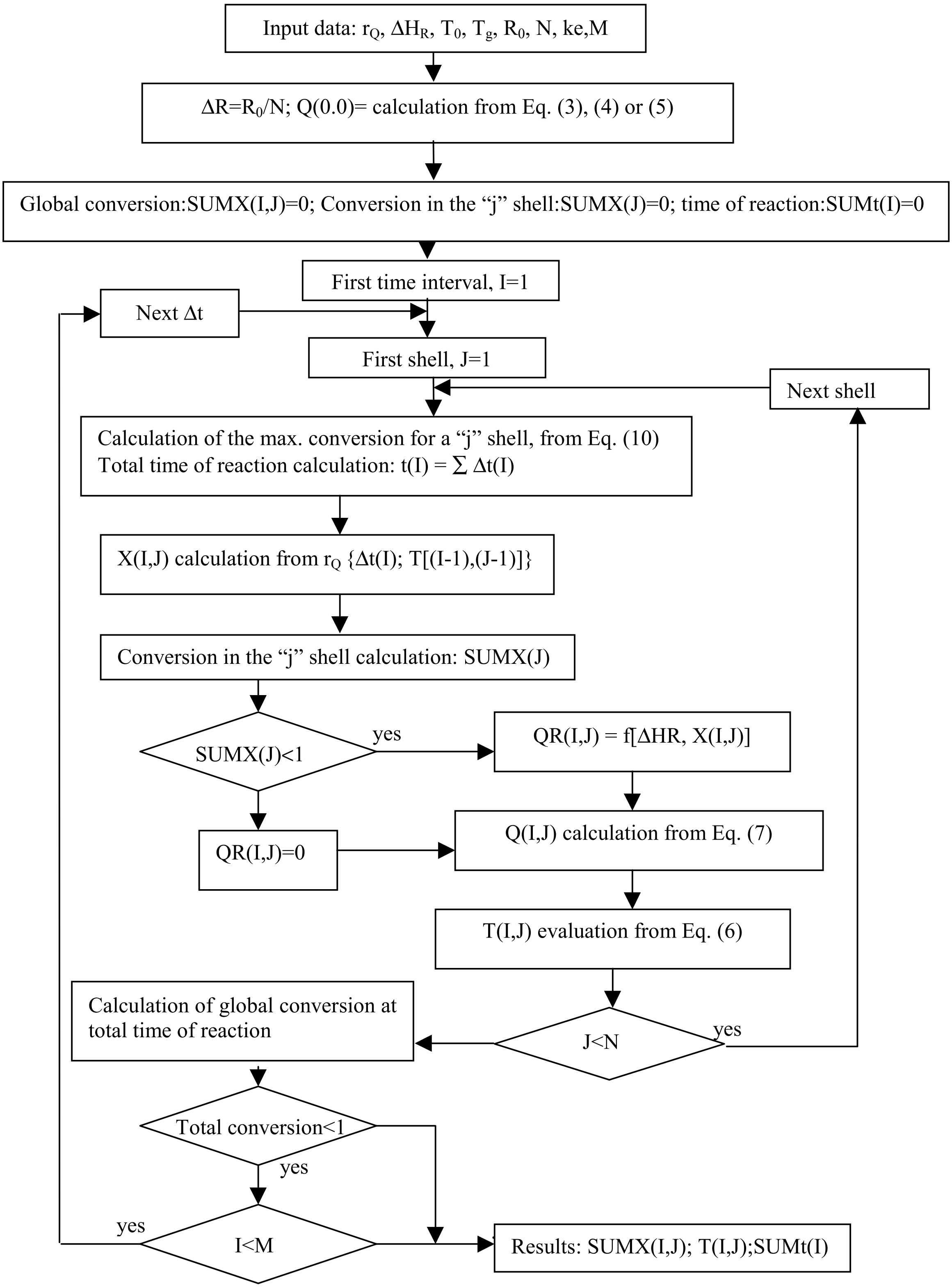

Fig. 2– Calculation flow chart for a gas-solid non catalytic reaction belonging to the progressive conversion model.

Argentina, and limestone from Neuquén, Argentina) was studied. The chemical composition and physical properties of these natural carbonates are summarized in Table 1.

Table 1. Chemical composition and physical properties of natural carbonates

	1	2	3	4
CaO (%)	≤29.00	≤53.00	≤49.00	≤50.00
MgO (%)	≤18.00	≥1.00	≥2.00	≥1.00
SiO_2 (%)	≥2.50	≥1.50	≥2.50	≥2.00
R_2O_3 (%)	≥2.00	≥1.50	≥2.50	≥3.50
S (%)	≥0.050	≥0.030	≥0.050	≥0.025
P (%)	≥0.010	≥0.010	≥0.030	≥0.010
R_2O (%)	≥0.10	≥0.10	≥0.10	≥0.10
H_2O (%)	≥2.00	≥2.00	≥2.00	≥2.00
Sp. area (m^2/g)	1.02	0.271	7.3	2.00
Porosity (%)	5.04	4.75	30.82	12.1

1: Dolostone (San Juan, Argentina). 2: Limestone (San Juan, Argentina). 3: Limestone (Neuquén, Argentina). 4:Travertine (San Juan, Argentina).

The equipment used to carry out the experimental program is detailed elsewhere (Silva *et al.*, 2000) and basically consists on four K type thermocouples (ϕ =1.5 mm), placed at different depths (T_{c0} at R_0= 35 mm, T_{c1} at R_1=25 mm, T_{c2} at R_2= 15 mm and T_{c3} at R_3= 5 mm) in a spherical sample (radius R_0= 35 mm) of the carbonate under study. This arrangement is placed in a muffle oven, in a position which ensures that heat will flow under isometric thermal conditions. In this way, the isothermal surfaces are spheres concentric with the sample.

The number of thermocouples used was four, because this quantity allows identifying the shape of the temperature profile, without causing an important perturbation in the system under study. Besides, although a bigger number of thermocouples would allow to obtain a more complete temperature profile, this could put in danger the mechanical stability of the sample, because it could crumble during the processes of shaping (to give it spherical form) or drilling (to insert the thermocouples).

According to Bird (1980), h_c can be determined from a semi empirical equation, which is valid for a single sphere of diameter D in a large body of fluid.

$$\frac{h_c D}{k_f} = 2 + 0.60 \left(\frac{D^3 \rho^2 g \beta \Delta T_{gs}}{\mu^2} \right)^{1/4} \left(\frac{Cp\mu}{k} \right)^{1/3} \qquad (13)$$

μ: Fluid viscosity [(Nt * s)/ m^2]
ρ: Fluid density [kg/m^3]
C_p: Heat capacity at constant pressure by mass unit
g: Gravitational acceleration, 9.80665 [m/s^2]
β: Thermal coefficient of volumetric expansion, ($1/T_f$) for ideal gases
k_f: Thermal conductivity of the fluid phase
ΔT_{gs}: Temperature difference between gas and solid phase [K]

In this equation the subscript "f" means that the fluid properties are evaluated at film temperature (T_g+T_{s0})/2. For a fluid without motion, as in the system under study, (h_c D/k) is equal to 2 and from this, h_c can be determined.

For temperatures below the thermal decomposition temperature (e.g. 623 K), temperature profiles show similar characteristics in all studied samples. Thermocouple temperatures are related by Eq. (6) and correspond to a constant heat flow through concentric spherical surfaces in which thermocouples are inserted. This is something expected, since there is no chemical reaction at these temperatures, then, there is no generation or absorption of heat in any point of the solid sample (Fig. 3A)

When the decomposition temperature of the carbonates is reached, different profiles are observed for the rocks studied. A similar behavior was observed in the thermal decomposition of carbonates from San Juan, Argentina. The curves obtained for these temperatures are shown in Fig. 3B, 3C and 3D. The curves fit the predictions of the mathematical model for reaction systems belonging to the unreacted core model.

In the case of limestone from Neuquén, which has different geological genesis from that of San Juan, the temperature profile observed during the thermal decomposition is different from those obtained for natural carbonates from San Juan. In this regime, temperature differences were observed in all shells limited by the inserted thermocouples. This is predicted by the mathematical model proposed for reaction systems in which the chemical reaction takes place simultaneously in the whole sample (progressive conversion model).

Following the calculation procedures proposed in Fig. 1 and 2, C^{++} codes were written in order to predict the temperature profile and its variation with time of reaction, when a gas-solid non-catalytic reaction is being carried out.

A comparison between the predictions of the model and the temperature profiles observed is presented only for the thermal decomposition of dolostone,

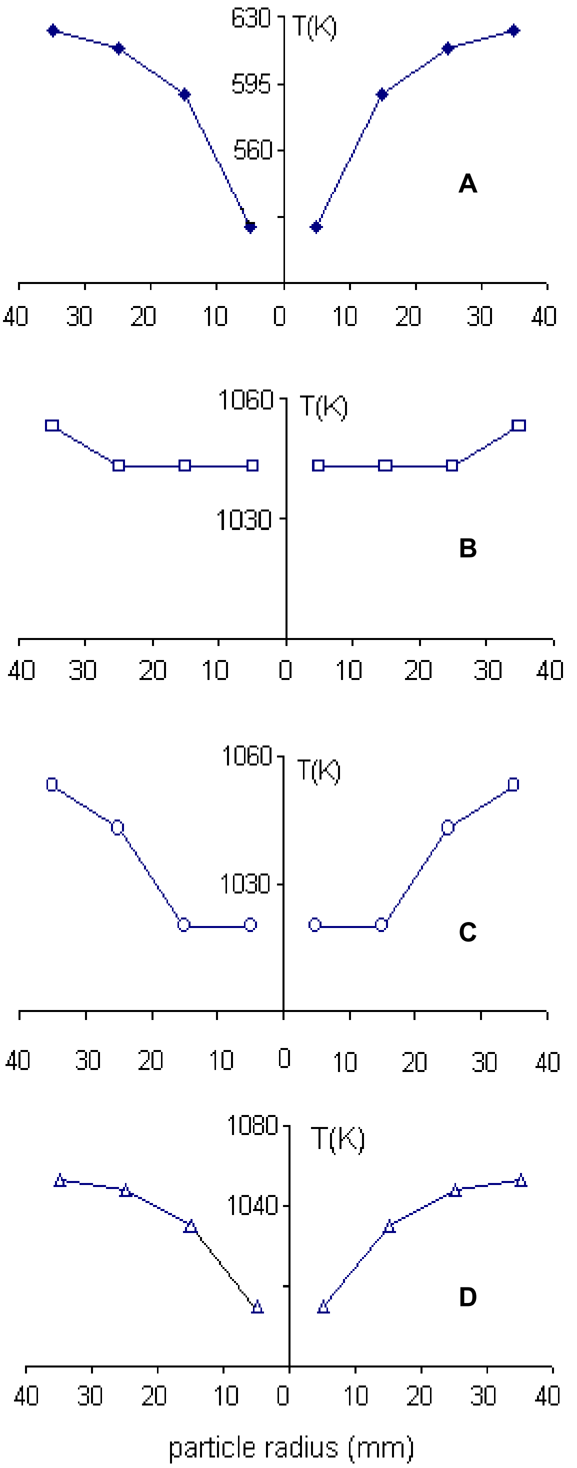

Fig. 3- Variations of the temperature profile with time: chemical reaction belonging to the unreacted core model.

because the chemical reaction kinetics (Silva *et al.*, 1999) and the thermal conductivities of the solid reactant and product (Silva *et al.*, 2000), are available only for that rock.

The reaction time was calculated from kinetics studies by means of the following equation, formely developed (Silva *et al.*, 1999):

$$t = \frac{2.89\left[(1-X)^{-0.5}-1\right]}{\eta^{0.5} P_0 A \exp(-S/T)} \tag{14}$$

where:

t: Reaction time (min)

P_0: Initial mass of the sample (g)

T: Reaction temperature (K)

S= -16965.3 K

A= 90536 exp (-0.2152 R_0) (g^{-1} min^{-1})

X: Fractional conversion

η: Mass fraction of carbonate in the stone ($gCO_3Ca.CO_3Mg/g$ dolostone)

The thermal conductivity of calcined and non-calcined dolostone was determined experimentally. The description of the experimental equipment, and the results were detailed previously (Silva *et al.*, 2000). The values obtained were:

$k_{non\text{-}calc.}$ = (3.175+/- 0.004) (J m/m^2 s K)

$k_{calc.}$ = (1.137 +/- 0.001) (J m/m^2 s K)

The emissivity was obtained form bibliography (Hewson *et al.*, 2001). A mean value of 0,85 was used.

The interval of time in which T_1= T_2= T_3, was compared with that predicted by kinetic studies for the thermal decomposition of the material limited by thermocouples T_{c0} and T_{c1}. A similar analysis was carried out for the time in which T_2 is equal to T_3. Experimental results differed from those predicted by the model in less than 12% as is shown in Table 2. This means that the mathematical model proposed, and the correlations used to calculate the parameters characterizing the transport of heat through the solid structure, are adequate to predict the behavior of the reacting system studied.

Table 2. Comparison of the time of reaction predicted by kinetic studies and by the proposed mathematical model for dolostones from San Juan (Argentina)

	Kinetic studies	Mathematical model
Shell (j=1)	22 (min)	19.7 (min)
Shell (j=2)	48 (min)	53.5 (min)

V. CONCLUSIONS

The calculation procedure presented here, which is conceptually simpler than others proposed for non-catalytic gas-solid reactions, is based on the energy balance when there is a constant heat flow between the fluid and the solid phase. In order to apply this procedure to a reaction system, the reaction kinetics, and the thermal conductivities of the solid reactant and product have to be known.

The analysis of temperature profiles in solid samples under chemical reaction, which is detailed here, seems an adequate tool to identify if a gas-solid reaction system belongs to the unreacted core model or to the progressive conversion one, provided that the thermal conductivity of the solid reactant is different from that of the solid product. A key feature in this proposal is the existence of a time interval in which the temperatures of the inner thermocouples are identical. This behavior was observed in the thermal decomposition of dolostone, travertine and limestone from San Juan and, according to the proposed mathematical model, can be explained only if the chemical reaction belongs to the unreacted core model.

The progressive conversion model is expected to fit for limestone from Neuquén, because there is no interval of time in which the equality of temperatures, $T_1=T_2=T_3$, is observed. This is for us a strong evidence that there is no unreacted core during the thermal decomposition of this rock, and that the reaction rate is different at different depths.

Once the kinetic model for a particular system has been selected, the calculation programs proposed here allow determining the conversion reached at a given reaction time.

The proposed mathematical model, and the calculation programs above mentioned, have been applied to the thermal decomposition of dolostone from San Juan (Argentina). Reaction times obtained from thermogravimetric studies of the thermal decomposition of dolostones, and those obtained by the calculation procedure presented here, disagree in less than 12%. This indicates that the proposed model is adequate for this reaction system, and that could be applied to another non-catalyzed solid-gas reactions such as thermal decompositions and sulfur roasting.

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Received: March 25, 2003.
Accepted for publication: October 8, 2003.
Recommended by Subject Editor Gregorio Meira