

Determination of Reaction Coefficient, Thermal Conductivity and Pore Diffusivity in Decomposition of Limestone of Different Origin

Duc Hai Do, Eckehard Specht

Abstract— This paper presents a method to evaluate the reaction rate coefficient, the pore diffusivity and the thermal conductivity of the lime layer in the decomposition of limestone of various origins with an analytical solution, based on the shrinking core model. Long cylindrical limestone samples with diameters greater than 20 mm were prepared and thermally decomposed in a chamber furnace at constant temperature and CO₂ pressure. By weighting and simultaneous measuring of the internal temperature, the decomposition behavior of these samples was studied. The reaction rate coefficients obtained vary from 0.003 to 0.013 m/s. The thermal conductivity lies between 0.52 and 0.83 W/m/K and the effective thermal conductivity changes with a factor of 12. The evaluated values by other authors based on limestone powder lie within this range. Besides, numerical solutions have been employed to simulate the effects of the material property on the decomposition behavior.

Keywords— Limestone decomposition; Reaction coefficient; Pore diffusivity; Thermal conductivity.

I. INTRODUCTION

Limestone (CaCO₃) is an important natural raw material in many branches of industry. Before final utilization, a large part of limestone must be calcinated in shaft or rotary kilns, where carbonate is thermally decomposed, splitting of CO₂ and yielding quick lime, which can be used, for example, in desulphurizing flue gas, in metallurgy, in construction.

The endothermic decomposition consists of five sub-processes, Fig.1: a) heat transfer from ambient to the solid surface, b) heat conduction from surface to the reaction front, c) chemical reaction at the front, d) diffusion of CO₂ through the porous oxide layer to the surface and e) the mass transfer into surroundings. The heat and mass transfer between fluid and solid have already been adequately investigated for flows and around individual bodies and in chemical apparatus such as, for example, packed beds. In

most books on heat transfer, e.g. Mills (1999), the equations are given. However, it is difficult to measure the reaction coefficient, the thermal conductivity and the pore diffusivity of CO₂ in the lime layer during calcination.

According to the knowledge of the authors, nearly all researchers have studied the material properties of limestone decomposition, using limestone particle in millimeter or micrometer range to exclude the influences of thermal conduction, pore diffusion, heat and mass transfer. Hu and Scorani (2003) conducted experiments with pulverized limestone about 60 μm and obtained reaction coefficient of 0.11 mol/m²/s and thermal conductivity from 0.10 to 0.86 W/m/K. Borgwadt (1989) measured two types of limestone based on 1 μm powder, and conducted that the reaction rate coefficient at 850°C is 0.012 mol/m²/s. Fuertes et al. (1993) conducted experiments over a size range of 0.25 -1.85 mm in a fluidized bed. Their result was 0.077 mol/m²/s at 850°C. Using a thermogravimetric analyzer under isothermal and non-isothermal conditions, Khinast (1996) studied the pore diffusivity and the reaction rate by using limestone powders ranging from 5 to 100 μm. Moffat and Walmsey (2006) carried out experiments at temperature 850 – 1200 °C and limestone particle size 5 – 25 mm. The thermal conductivity obtained lies between 0.1 and 1.5 W/m/K. Under ambient conditions with CO₂ concentration from 0 to 80 % and limestone particle size from 0.4 to 2.0 mm, Fuertes et al. (2002) evaluated the reaction coefficient varying from 0.6 to 3 mol/m²/s.

In the above researches, the experiments were conducted using limestone particle in millimeter or micrometer range. However, in the lime industry the limestone pieces of centimeters are usually burnt. Therefore the experiments were conducted using pieces with diameter bigger than 10 cm to evaluate their property. The result of this study is useful for lime industry to understand the effect of the limestone origin on the decomposition behavior and the lime quality

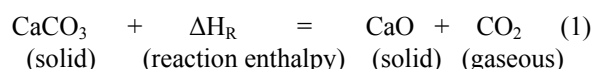
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II. DECOMPOSITION MODEL

The decomposition of limestone is an endothermic topochemical reaction:



The calcination process can be explained using a partially decomposed piece of carbonate, whose profiles of CO₂ partial pressure and temperature are shown in Fig. 1. The specimen comprises a dense carbonate core surrounded by a porous oxide layer. In the calcination reactor at temperature T_g heat is transferred by radiation and convection (symbolized by α) to the solid surface at a temperature of T_w. By means of thermal conduction (λ) heat penetrates through the porous oxide layer to reach the reaction front, where the temperature is T_f. As the reaction enthalpy is many times greater than the internal energy, the heat flowing further into the core is negligible during reaction. Therefore the core temperature is only slightly lower than the front temperature. Once heat is supplied, the chemical reaction (k) then takes place, for which the driving force is the deviation of CO₂ partial pressure from the equilibrium (p_{eq} - p_f). The released CO₂ diffuses (D^p) through the porous oxide layer to the surface and finally passes by convection (β) to the surroundings where the CO₂ partial pressure p_g exists.

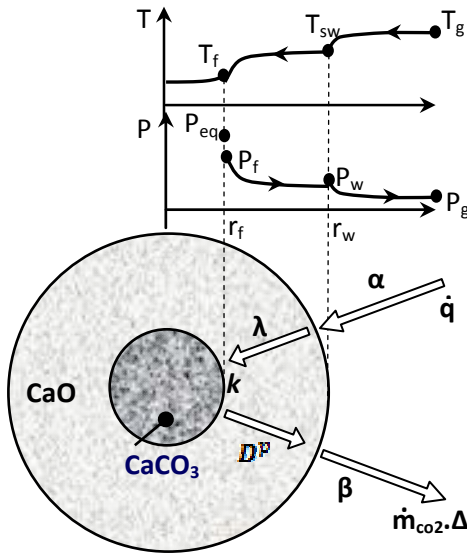


Fig. 1. Model of limestone decomposition

A one-dimensional shrinking core model can be established based on the assumptions of ideal sample geometry such as sphere, cylinder or plate, a homogeneous chemical composition and structure in the sample, and a symmetrical heat supply. The reaction starts uniformly on the solid surface, always forming a smooth reaction front, which then processes continuously into the interior. Based on the shrinking core model, Szekely et al. (1976) and Kainer et al. (1986) have derived a couple of differential equations to calculate the decomposition temperature (T_f) and the conversion degree (X) depending on time t as:

$$\frac{dX}{dt} \cdot [R_{\alpha} + R_{\lambda} \cdot f_1(X)] = 1 \quad (2)$$

$$\frac{dX}{dt} \cdot [R_{\beta} + R_D \cdot f_1(X) + R_k \cdot f_2(X)] = 1 \quad (3)$$

where the form functions $f_i(X)$ are given by Kainer et al. (1986) and the resistances R_i are described as below.

$$R_{\alpha} = \frac{K_C \cdot \Delta h_R}{T_g - T_f} \cdot \frac{r_w}{\alpha \cdot b} \quad (4)$$

$$R_{\lambda} = \frac{K_C \cdot \Delta h_R}{T_g - T_f} \cdot \frac{r_w^2}{2 \cdot \lambda \cdot b} \quad (5)$$

$$R_k = \frac{K_C \cdot R_C \cdot T_f}{p_{eq} - p_g} \cdot \frac{r_w}{k} \quad (6)$$

$$R_D = \frac{K_C \cdot R_C \cdot T_f}{p_{eq} - p_g} \cdot \frac{r_w^2}{2 \cdot D^p \cdot b} \quad (7)$$

$$R_{\beta} = \frac{K_C \cdot R_C \cdot T_f}{p_{eq} - p_g} \cdot \frac{r_w}{\beta \cdot b} \quad (8)$$

Here K_C is the mass fraction of CO₂ in the limestone, Δh_R the specific reaction enthalpy, b is the shape factor and P_{eq} is the equilibrium pressure described by Silva et al. (2010).

$$P_{eq} = 2.15 \cdot 10^7 \cdot \exp\left(-\frac{168 \text{ kJ/mol}}{R \cdot T_f}\right) \quad (9)$$

III. EVALUATION METHOD

Further experiments with other sizes have shown that the temperature at the reaction front T_f changes only slightly during decomposition under constant ambient conditions (p_f and T_f), especially when $0.1 < X < 0.9$, by H. Kainer et al. (1986). Therefore, the corresponding equilibrium pressure p_{eq} and resistances R_i remain virtually constant during decomposition. Therefore, two linear equations used to calculate the material properties can be described by these authors as:

$$\frac{t}{f_3(X)} = R_{\alpha} + R_{\lambda} \cdot \frac{f_4(X)}{f_3(X)} \quad (10)$$

$$\frac{t - R_{\beta} \cdot f_3(X)}{f_5(X)} = R_k + R_D \cdot \frac{f_4(X)}{f_5(X)} \quad (11)$$

The experimental determination of desired values requires constant ambient conditions and measurement of time dependent progress of conversion degree (by weighing, for example) and the front temperature (by thermal couples, for example).

IV. EXPERIMENTAL SET UP

The experimental apparatus for measuring the decomposition behavior is shown schematically in Fig. 2. The limestone specimens were suspended from a balance with which the weight loss and therefore the conversion degree could be recorded continuously. The specimen was enclosed within a cylindrical flow channel

mounted in an electrically heated chamber furnace whose temperature was kept constant gas was introduced at the top of the channel and sucked off at a defined rate from the bottom. This prevented an enrichment of CO₂ in the channel, so that the ambient partial pressure of CO₂ was kept constant. In the center of the specimen small holes were drilled. The temperatures inside the specimen were measured by thermocouples inserted in the holes. These were mounted at the center for all the specimens involved, and also at the periphery for some specimen. The wall temperature of the channel was measured at various positions with thermocouples, whose measurements showed that the channel had a uniform temperature.

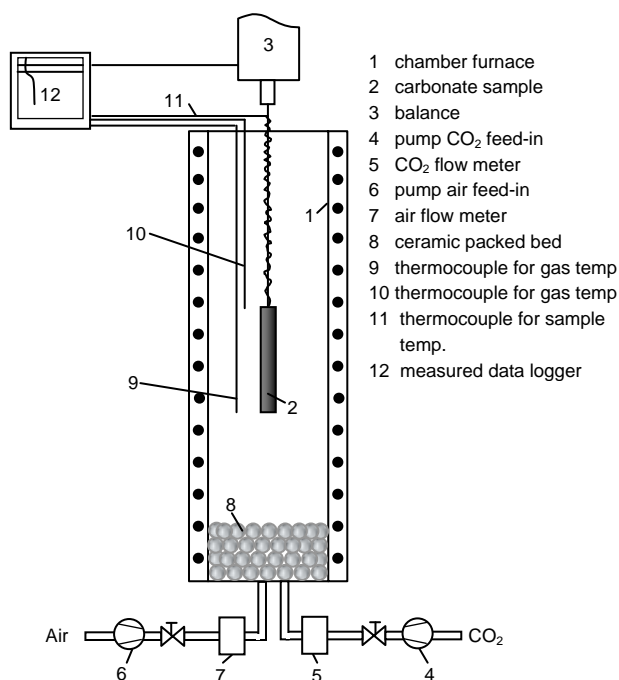


Fig. 2. Experimental apparatus for measuring limestone decomposition

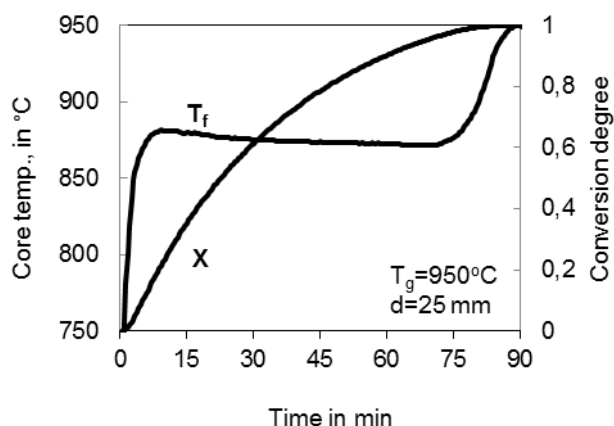


Fig. 3 Typical conversion curves

V. EXPERIMENTAL RESULTS

As an example, Fig. 3 shows typical curves of the conversion X and the core temperature T_f for a cylindrical limestone specimen with a diameter d=25 mm and at ambient temperature, T_g=950 °C. At temperatures below 750 °C, the heat supplied was first used only for raising rapidly the internal energy of the specimen and there is no substantial decomposition occurred. After the heating-up of the specimen had been accomplished, the equilibrium pressure and the decomposition rate became so great that the heat transported to the specimen was consumed virtually only by reaction. The temperature in the carbonate core was then nearly uniform. After completion of decomposition the core temperature finally rose until the ambient temperature and a steady state was established.

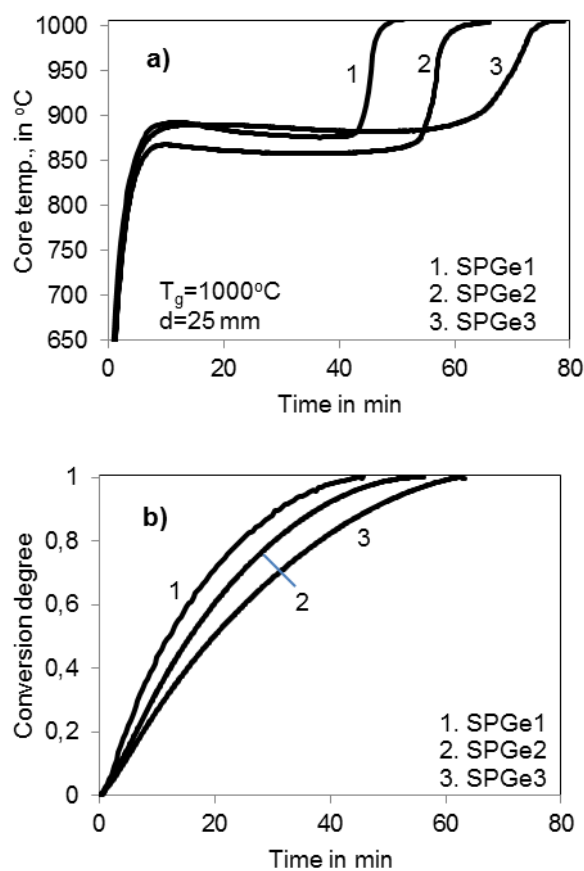


Fig. 4 Core temperatures (a) and conversion degree (b) of different limestones

Similarly, the limestones from three origins in Germany were thermally decomposed at the same ambient condition in order to compare their properties. The experimental results are shown in Fig. 4a and Fig. 4b for the core temperature and the conversion degree, respectively. It can be seen that the decomposition behaviors are different. This is due to the different of limestone properties of different origins, which will be discussed later.

VI. MATERIAL PROPERTIES

The measured conversion curves for the decomposition degree were linearized in accordance with Eq. (4) and (5). As an example, Fig. 5 shows such diagrams for a cylindrical specimen as an example. It is obvious that the measured values can be satisfactorily approximated by straight lines, and thus in turn confirms the validity of the equations established above. From the ordinate intercept the reaction rate coefficient and the overall heat transfer coefficient can be determined using Eqs. (6) and (4), respectively, and from the slopes the effective pore diffusivity and the thermal conductivity can be calculated using Eqs. (7) and (5) respectively

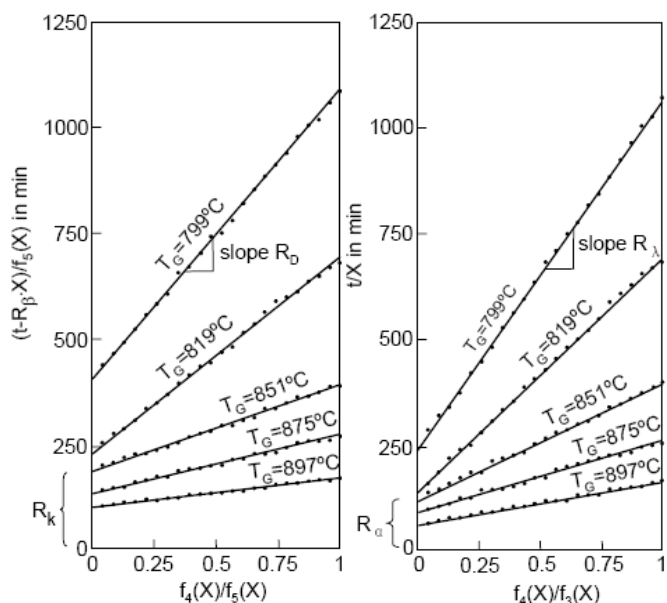


Fig. 5. Linearized decomposition diagrams

Table 1. Solid material properties

| Origin | $k \cdot 10^{-2}$ [m/s] | λ [W/m/K] | $D^p \cdot 10^{-4}$ [m ² /s] |
|--------|-------------------------|-------------------|---|
| SPGe1 | 0.71 | 0.81 | 1.63 |
| SPGe2 | 0.93 | 0.65 | 1.28 |
| SPGe3 | 0.58 | 0.72 | 2.4 |

The evaluation method is applied to evaluate the material properties of limestone samples. Table 1 summarizes the values of reaction coefficient, thermal conductivity and pore diffusivity of samples mentioned in Fig. 4.

In Fig. 4, it is clear that the total decomposition time of limestone strongly depends on the limestone origin. This is due to the differences of material properties summarized in Table 1. Cheng and Specht (2006) also studied these properties of different limestone origins and the results showed that the thermal conductivity and the reaction rate are dominant factors effecting on calcination time while the effective pore diffusivity has low influence. In Table 1, the sample SPGe3 has the smallest values of reaction coefficient of 0.005 m/s, resulting in the longest reaction time of 78 min. The larger the reaction coefficient, the shorter is the calcination time. The thermal conductivity also has similar

effect on the calcination time. The larger the thermal conductivity, the shorter is the calcination time. This can be seen from the sample SPGe1 with the largest values of thermal conductivity of 0.81 W/m/K, leading to the shortest reaction time of 52 min.

In this study, other limestone pieces of different origins in Germany were prepared with 25 mm diameter and thermally decomposed at ambient temperature of 1050 °C. The evaluation results are shown in Table 2.

In Table 2, it can be seen that the reaction coefficient varies in the range from 0.003 to 0.013 m/s, the thermal conductivity lies in between 0.52 and 0.83 W/m/K and the pore diffusivity changes with a factor of 12. The reaction coefficient obtained from the literatures mentioned above varies with a factor of 4, from 0.003 to 0.012 m/s and the thermal conductivity lies between 0.5 and 1.3 W/m/K. That means our values lie within these ranges, which demonstrates that the evaluation method is reliable.

Table 2. Material properties of different limestones

| Origin | $k \cdot 10^{-2}$ [m/s] | λ [W/m/K] | $D^p \cdot 10^{-4}$ [m ² /s] |
|------------|-------------------------|-------------------|---|
| Origin SPA | | | |
| Ge.SPA1 | 0.40 | 0.70 | 2.3 |
| Ge.SPA2 | 0.61 | 0.68 | 0.62 |
| Ge.SPA3 | 0.71 | 0.71 | 3.4 |
| Origin SPB | | | |
| Ge.SPB1 | 0.82 | 0.78 | 4.5 |
| Ge.SPB2 | 0.56 | 0.73 | 2.6 |
| Ge.SPB3 | 0.38 | 0.81 | 4.3 |
| Origin SPC | | | |
| Ge.SPC1 | 0.76 | 0.52 | 6.3 |
| Ge.SPC2 | 1.26 | 0.64 | 7.1 |
| Ge.SPC3 | 0.91 | 0.58 | 2.5 |
| Origin SPD | | | |
| Ge.SPD1 | 0.42 | 0.82 | 5.3 |
| Ge.SPD2 | 0.33 | 0.83 | 4.1 |
| Ge.SPD3 | 0.31 | 0.80 | 3.6 |

VII. INFLUENCES OF MATERIAL PROPERTY ON DECOMPOSITION

To see the influence of material properties on the decomposition behavior, especially the decomposition temperature, that is a dominant factor for lime reactivity. Numerical solutions have been developed to solve a couple of differential equations (3) - (4) to calculate the decomposition temperature and conversion degree depending on time. The input parameters of the limiting values are taken from the experiential evaluations as mentioned before. A cylindrical particle of 30 mm diameter reacting at constant ambient temperature of 1000 °C is

considered. In Fig. 6 the surface temperature (w) and the front temperature (f), which is similar to the core temperature, are plotted versus time for a large and low reaction coefficient, respectively. The higher the reaction coefficient, the shorter is the reaction time. For these two values, the time is shorted by 35 min. This figure also shows that a larger reaction coefficient needs a lower front temperature because the decomposition pressure as driving force is required lower.

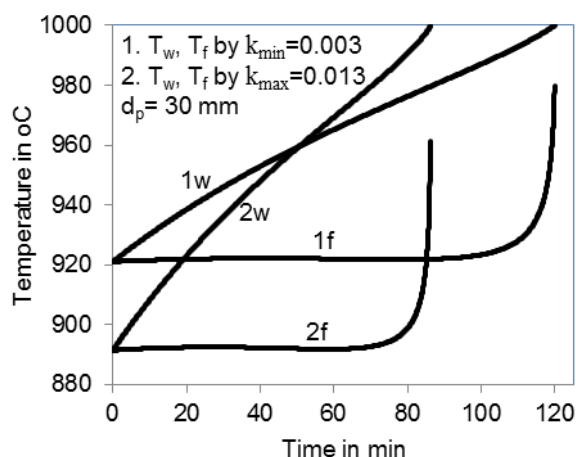


Fig. 6. Influences of reaction coefficient on lime temperature

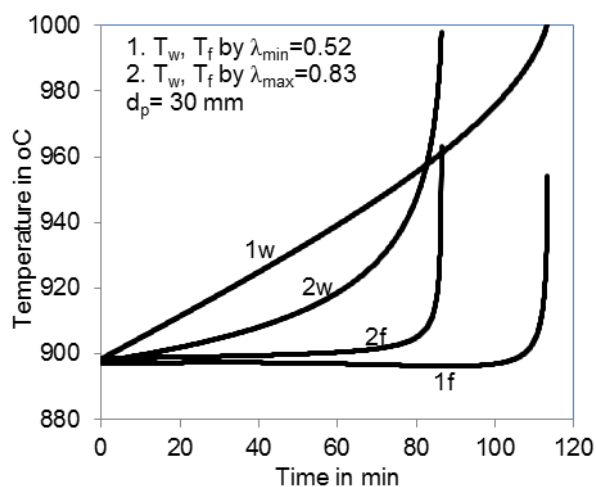


Fig. 7. Influences of thermal conductivity on lime temperature

The influence of the thermal conductivity on the temperature is illustrated in Fig. 7 in the same manner with the two limiting values. The higher the thermal conductivity, the shorter is again the decomposition time. For these two values, the decomposition time is reduced by 30 min. It can be also revealed that a higher conductivity needs a lower temperature as driving force. This results in a higher front temperature and a lower surface temperature.

VIII. CONCLUSIONS

The limestone specimens of different origins were thermally decomposed under constant ambient conditions. The weight loss and the core temperature were simultaneously recorded. The material property can be determined by the analytical solution based on linearizing the conversion curves. The reaction rate coefficient, the thermal conductivity and the effective pore diffusivity are calculated from the slopes and the ordinate intercepts of the linearized curves.

The reaction rate coefficient varies with a factor of 4 from 0.003 to 0.013 m/s. The thermal conductivity lies between 0.52 and 0.83 W/m/K while the effective pore diffusivity varies with a factor of 12. These results are consistent with the results published in previous literatures, in which fine limestone powder were examined. The reaction rate coefficient and the thermal conductivity have dominant effects on the decomposition behaviour of the limestone.

The numerical solution was employed to study the influence of the material property on the decomposition temperature. High values of reaction coefficient cause low decomposition temperatures, low values results in high decomposition temperatures. On the other hand, the higher the thermal conductivity, the higher will be the decomposition temperature.

NOMENCLATURE

| | |
|----------|--|
| b | shape factor |
| D^p | pore diffusion coefficient [m ² /s] |
| f | form factor |
| k | reaction rate coefficient [m/s] |
| K_C | mass fraction of CO ₂ in carbonate [kg/m ³] |
| P | pressure, [Pa] |
| P_{eq} | equilibrium pressure, [Pa] |
| r | position coordinate, radius [m] |
| R | universal gas constant, [J/mol/K] |
| R_C | special gas constant of CO ₂ , [J/mol/K] |
| R_i | resistance sub-process, [s] |
| t | time, [s] |
| T | temperature, [K] |
| X | conversion degree |

Greek symbols

| | |
|--------------|---|
| α | heat transfer coefficient, [W/m ² K] |
| β | mass transfer coefficient, [m/s] |
| λ | thermal conduction coefficient, [W/mK] |
| Δh_R | specific reaction enthalpy, [J/kg] |

Subscripts

| | |
|---|-------------------|
| C | CO ₂ |
| D | diffusion |
| F | reaction front |
| G | ambient |
| k | chemical reaction |
| R | reaction |
| W | surface, wall |

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