

*Dedicated to Professor Valer Fărcășan  
at his 85<sup>th</sup> anniversary*

## **MODELING AND SIMULATION OF CALCIUM CARBONATE THERMAL DECOMPOSITION IN THE VERTICAL LIME KILN BASED ON THE SHRINKING UNREACTED CORE MODEL**

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**ABSTRACT.** The paper presents the dynamic simulation results obtained by modelling the vertical lime kiln for thermal decomposition of limestone. The simulator relies on the rate controlling heat balance equations describing the advance of the reaction front in the spherical limestone boulder, according to the shrinking unreacted core model. The vertical lime kiln is considered to be divided in three distinct zones along the moving flux of the solids: heating, reaction and cooling zone. Each of the zones are described by the limestone boulder travelling down along the kiln height. Results reveal the time and space distribution of temperature in the lime kiln for both solids and gases, based on the time and space distribution of the temperature in the limestone boulder and the gases surrounding it. The dynamic simulator serves as a useful tool for investigating the way that lime kiln may be operated and controlled for improved performance.

### **1. INTRODUCTION**

Thermal decomposition of limestone has been of large interest over the past, as both calcium oxide and carbon dioxide are basic raw materials for a large range of products in chemical or construction material industries. Despite the important advances performed in process equipment design, the vertical lime kiln remains one of the main units for performing the industrial scale calcium carbonate decomposition.

Developments of information technology and computer sciences, during the last decades, make possible the study and investigation of the limestone decomposition by simulation. The continuous growing complexity of the dynamic models is supported by specific software tools allowing a thorough analysis of the process with direct effects on the improvement of the product yields.

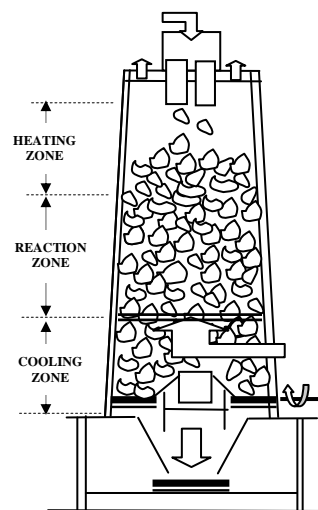
Results of the presented dynamic simulator emerge from a different approach for solving the mathematical model of the lime kiln simulator presented in earlier studies [1], [2].

The vertical lime kiln under study is presented in figure 1. It is considered to have three distinct zones along the direction of transport of the solids moving in counter-current with the gaseous flux.

The heating zone is the place where the solid phase temperature is increased up to the decomposition conditions (temperature around 900 °C) by the help of the gases coming from the reaction zone. In the reaction zone hot gases emerged from the fuel combustion provide the necessary heat for the endothermic decomposition process (temperature exceeding 900 °C) and for the previous limestone preheating step. The third zone is the cooling one where solids temperature is reduced and the inlet combustion air flux is preheated from the ambient temperature. The products of the vertical kiln are the lime flux evacuated at the bottom of the kiln and the gaseous flux exhausted at the top of it, having rich 35-40 vol. %, carbon dioxide concentration.

Due to the large dimensions, the lime kiln dynamic behaviour exhibits important time constants and considerable dead time resulting in negative impact on the controllability of the decomposition process. As a consequence, it is important to investigate the dynamic behaviour and the influence of different operating parameters or disturbance factors for the benefit of improved operation of the industrial unit.

Figure 1. Vertical kiln scheme.



## 2. MATHEMATICAL MODEL DESCRIPTION

The mathematical model is developed based on the large accepted considerations that heat transfer is the rate-controlling step of the process [1], [2].

In order to describe the macroscopic behaviour of the kiln in its three aforementioned zones, phenomena taking place in a limestone spherical boulder is investigated. The shrinking unreacted core model has been chosen to reflect the complex heat and mass transfer processes taking place during limestone decomposition [1]. Nevertheless, the mathematical model takes into account several simplifying assumptions. They are: the limestone is uniformly distributed across the kiln section and the circulation regime is ideal for both the solid and the gaseous phase; the limestone boulders are spherical shaped and have homogenous initial properties, such as: constant and identical diameters, uniform external surface temperature, reaction surface propagation within the limestone boulder has a spherical symmetry; heat capacity, density and thermal conductivity of both calcium carbonate and calcium oxide are temperature independent; properties of the gaseous phase may be considered constant for each of the three kiln zones.

These assumptions lead to the following equations.

1. For the heating and the cooling zone:

- within the solid boulder the heat transmitted by conduction is described by the one-dimensional model with spherical symmetry:

$$\frac{\partial T_s}{\partial t} = a \left( \frac{\partial^2 T_s}{\partial r^2} + \frac{2}{r} \frac{\partial T_s}{\partial r} \right), \quad (1)$$

- in the gaseous phase the heat transferred between the solid surface and the gases is described by the equation:

$$\frac{dT_G}{dt} = k_T S_V (v_S / w_G) (T_G - T_{Sp}). \quad (2)$$

These equations have associated the following initial and boundary conditions:

$$\begin{aligned} t = 0, \quad 0 \leq r \leq R; \quad T = T_0, \quad T_G = T_{G0} \\ t > 0; \quad r = R, \quad T = T_{Sp}, \quad \lambda \frac{\partial T}{\partial r} = k_T (T_G - T_{Sp}) \\ r = 0; \quad \frac{\partial T}{\partial r} = 0 \end{aligned} \quad (3)$$

2. For the reaction zone the main phenomena taking place are: heat transfer by convection and radiation from the gaseous phase to the solid phase surface, heat transfer by conduction through the already formed calcium oxide layer, chemical reaction in the dissociation layer, carbon dioxide diffusion from the reaction layer to the gaseous phase associated with its heating up to the gaseous phase temperature and heating the unreacted limestone core up to the decomposition temperature. The equations for this zone describe:

- the heating of the unreacted limestone core:

$$\frac{\partial T_2}{\partial t} = a_2 \left( \frac{\partial^2 T_2}{\partial r^2} + \frac{2}{r} \frac{\partial T_2}{\partial r} \right) \quad (4)$$

- the heating by conduction of the already formed calcium oxide layer together with the heating of the carbon dioxide contained in it:

$$\frac{\partial T_1}{\partial t} = a_1 \left( \frac{\partial^2 T_1}{\partial r^2} + \frac{2}{r} \frac{\partial T_1}{\partial r} \right) + \frac{M_{CO_2} c_{p(CO_2)} \rho_2}{M_{CaCO_3} c_{p(CaCO_3)} \rho_1} \frac{r_m^2}{r^2} \frac{dr_m}{dt} \frac{dT_1}{dr} \quad (5)$$

- the heat transfer between the solid surface and the gases, described by the equation (2).

The initial and boundary conditions associated with this zone are:

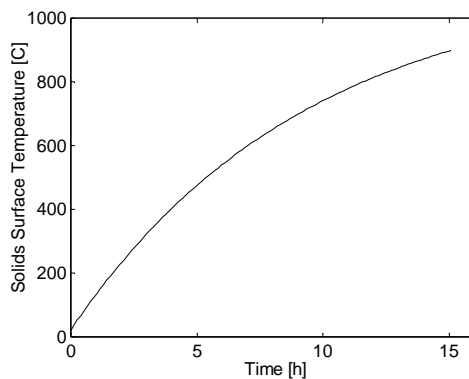
$$\begin{aligned} t = 0, \quad 0 \leq r \leq R; \quad T_1 = T_2 = T_0, \quad T_G = T_{G0} \\ t \geq 0; \quad r = R, \quad T_1 = T_S, \quad \lambda_1 \frac{\partial T_1}{\partial r} = k_T (T_G - T_S) \\ r = r_m; \quad T_1 = T_2 = T_d \quad \lambda_1 \frac{\partial T_1}{\partial r} + (\Delta H_R) \rho_2 \frac{dr_m}{dt} = \lambda_2 \frac{\partial T_2}{\partial r} \end{aligned} \quad (6)$$

Solving the set of time and space dependent system of partial differential equations has to face the challenge of the moving boundary feature. First the equations are scaled introducing dimensionless variables. For solving the scaled system of PDE equations the partial differential terms are replaced by finite difference terms using simultaneous discretization of both time and space independent variables. The moving boundary problem is managed by reconsidering the time discretization step (as the reaction layer advances) such as to preserve the space discretization network [1]. The emerged algebraic system of linear equations is solved using specific MATLAB software tools.

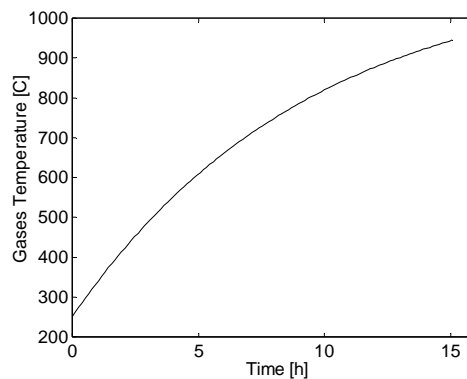
### 3. SIMULATION RESULTS

The investigation has been carried out for the case of a limestone boulder of spherical shape with a radius of 45 mm, considered as a typical case for the industrial practice [3].

The simulation results obtained for the solid surface temperature and for the gaseous phase temperature variations, in the heating zone, are shown in figure 2 and figure 3. They reflect the heating process taking place outside the limestone boulder as it passes over the heating zone.



**Figure 2. Solids surface temperature during the heating step.**

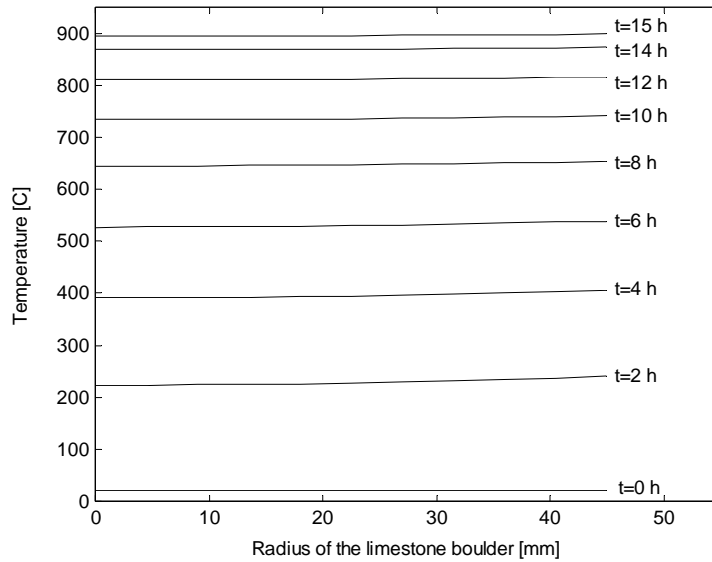


**Figure 3. Gases temperature during the heating step.**

The way temperature changes within the limestone boulder during the heating period, finished as soon as the surface temperature reaches the decomposition threshold, is presented in figure 4.

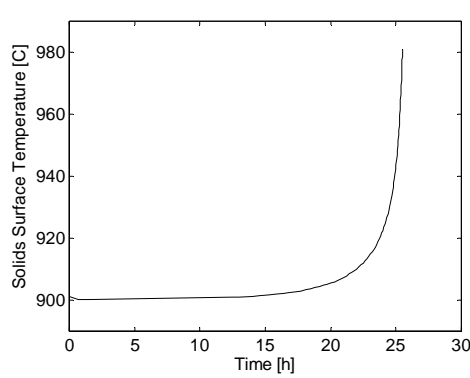
As it may be concluded from the presented figures, the time necessary for the limestone boulder to pass the heating zone and to reach the decomposition temperature is of  $t=15$  hours.

Further investigations have been carried out to determine the temperature variations of the limestone boulder passing the reaction zone.

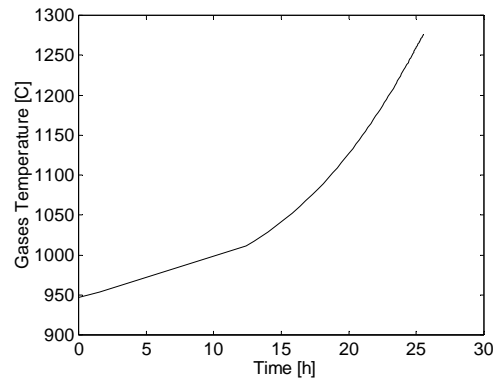


**Figure 4. Temperature change within the limestone boulder during the heating step.**

The simulation results obtained for the solid temperature (at different distances from the limestone boulder centre) and for the gaseous phase temperature, in the reaction zone, are shown in figure 5 and figure 6.

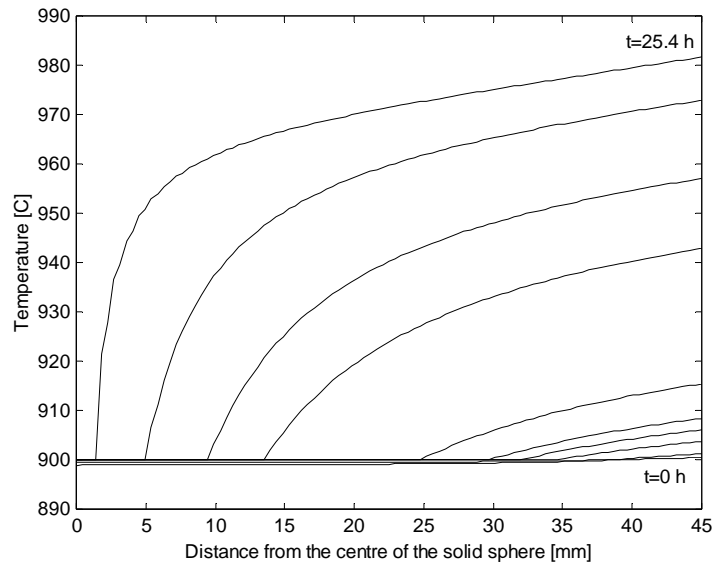


**Figure 5. Solids surface temperature during the reaction step.**



**Figure 6. Gases temperature during the reaction step.**

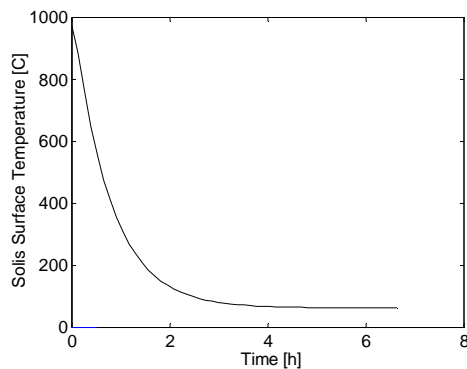
Figure 7 presents the temperature evolution along the distance from the centre of the limestone boulder during the reaction stage.



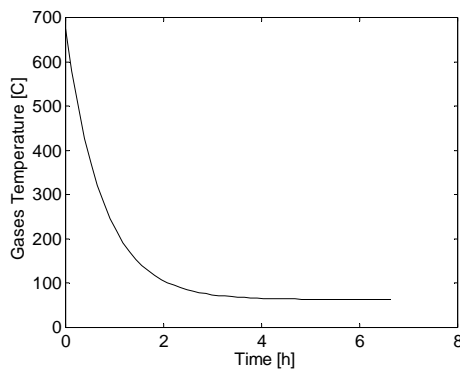
**Figure 7. Temperature changes within the limestone boulder during reaction step.**

The reaction stage extends over a period of  $t=25.5$  h. At temperatures exceeding  $900^{\circ}\text{C}$ , the lime porous structure presents a large specific surface leading to a fast decomposition of the limestone. For higher temperatures the occurrence of calcium oxide re-crystallisation determines a reduction of the specific surface hence leading to a diminished reactivity.

Finally, results for the cooling stage are presented in figure 8 and figure 9 for the solids surface (calcium oxide boulder) and for the surrounding gases temperature.

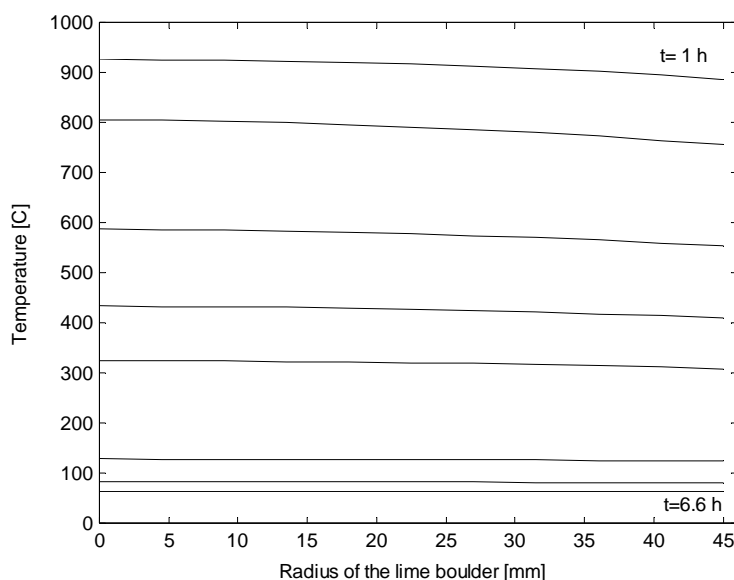


**Figure 8. Solids surface temperature during the cooling step.**



**Figure 9. Gases temperature during the cooling step.**

Temperature changes within the lime boulder during the cooling period of  $t=6.6$  h are shown in figure 10.



**Figure 10. Temperature changes within the lime boulder during the cooling step.**

As it may be noticed, the reaction stage is the most time consuming period of the limestone decomposition cycle while the cooling stage is smaller than the heating one.

Simulations reveal that due to the fact that properties of the limestone mineral have varying values, corresponding to various sources, the constants of the model equations have to be fitted to the particular source [4].

#### 4. CONCLUSIONS

The developed simulator gives the opportunity to investigate the dynamic behaviour of a chemical process taking place according to the shrinking unreacted core model, applied to the limestone decomposition.

Dynamic evolution of the reaction surface within the limestone-lime boulder allows the disclosure of gases and solids temperature profile along the limestone kiln using natural gas fuel introduced at the limit between the reaction and cooling zones. The moving boundary problem is solved using a special mathematical approach based on space and time discretization network, implementing an effective algorithm for solving the system of partial differential equations.

The simulation results for the 90 mm diameter limestone boulder show residence times of 15 h, 25.4 h and 6.5 h, for the three zones of the kiln, presenting a good fit with the industrial unit values of 15 h, 25 h and 9 h. Further development of

the simulator is possible and necessary in order to reveal changing operating conditions and variable distribution of limestone boulders dimensions.

The simulator serves as a useful tool for looking into the details of the limestone decomposition process for revealing ways for obtaining optimal operating regimes of the vertical kiln and also offering an application example for other processes evolving in accordance to the same mechanism.

## NOMENCLATURE

$a$  – thermal diffusivity [ $\text{m}^2/\text{h}$ ]  
 $c_p$  – heat capacity [ $\text{kcal}/\text{kg}\cdot\text{grd}$ ]  
 $k_T$  – heat transfer coefficient [ $\text{kcal}/\text{m}^2\cdot\text{h}\cdot^\circ\text{C}$ ]  
 $r$  – distance from the centre of the sphere [ $\text{m}$ ]  
 $t$  – time [ $\text{h}$ ]  
 $v_S$  – velocity of the limestone boulder [ $\text{m}/\text{s}$ ]  
 $v_G$  – velocity of the gases [ $\text{m}/\text{s}$ ]  
 $M$  – molecular mass [ $\text{kg}/\text{kmole}$ ]  
 $R$  – radius of the boulder sphere [ $\text{m}$ ]  
 $S_V$  – specific surface [ $\text{m}^2/\text{m}^3$  of the kiln]  
 $T$  – temperature [ $^\circ\text{C}$ ]  
 $w_G$  – heat capacity of the gaseous flux [ $\text{kcal}/\text{m}^2\cdot\text{h}\cdot^\circ\text{C}$ ]  
 $\Delta H_R$  – heat of reaction [ $\text{kcal}/\text{kg CaCO}_3$ ]  
 $\lambda$  – thermal conductivity [ $\text{kcal}/\text{m}\cdot^\circ\text{C}\cdot\text{h}$ ]  
 $\rho$  – density [ $\text{kg}/\text{m}^3$ ]

## Indices

1 – calcium oxide (lime)  
2 – calcium carbonate (limestone)  
 $m$  – core  
0 – initial  
 $G$  – gaseous phase  
 $S$  – solid phase  
 $p$  – surface

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