THERMOGRAVIMETRIC DETERMINATION OF THERMAL CONDUCTIVITY OF LUMPY LIMESTONES

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ABSTRACT

It is known that limestone from different origins decomposed at same kiln conditions produce either hard burnt or soft burnt lime. The reason was unknown. In the previous research, thermal conductivity is found to be one of the important thermal properties which determines the calcination behavior. In this research, lumpy limestone particles of various origins have been decomposed in the laboratory furnace. Cylindrical particles have been chosen in the size range between 14 mm to 33 mm. A hole is drilled at the center of each of the particle to insert the thermocouple. The particles are decomposed in the temperature range between 900 °C and 1200°C in a tube furnace. During the decomposition weight loss as well as the core temperature of the particles are measured and recorded simultaneously. The measured core temperature and the slope of the weight loss curves have been used as input to the model that is developed in addition to the kiln conditions. This shrinking core mathematical model developed can predict the thermal conductivity of lime obtained from various limestone. The experimental and modeling methods are described in this paper. To verify the results, thermal conductivity of few of these samples are measured using laser flash apparatus. The results obtained with these two different methods were very well matched. The thermal conductivity of lime measured using thermogravimetric decomposition method with lumpy limestone decomposition is representative of the limestones those are decomposed in the industrial kilns. The thermal conductivity of lime from various limestone were found to be in the range from 0.3 to 0.85 W/(mK).

INTRODUCTION

Lime is an important raw material in various industries. Lime is generally produced in shaft kilns or rotary kilns. Lime is used in different forms in wide range of industries for various purposes. Quality of the product lime is the major aspect of the process. Soft-burnt lime (lime produced under controlled conditions, such as at relatively lower temperatures) is generally highly reactive and has significant usage in certain industries such as steel industry. Whereas hard burnt lime (lime produced at high temperatures) is less reactive in nature and has its applications in some other branches of industry such as building industry. This is because the calcination process at higher temperatures causes sintering of the product (lime), which in turn reduces the internal surface area available for the reaction. So it is essential to understand the temperature distributions in the lime kiln in order to assure the better quality of the lime. In order to understand the product quality, several experimental and numerical studies have been conducted in the literature. Most of the research in the literature was carried out with the lime powder or limestone particles in the size range between 0.07-4 mm in size [1,2,3] some authors even worked with 5-10 µm particles [4,5].

Nomenclature

$\dot{Q}$	[W]	Rate of heat transfer
X	[-]	Conversion degree
k	[W/mK]	Thermal conductivity
$\dot{q}'''$	[W/m^3]	Volumetric heat generation density
R	[m^{2}K/W]	Interfacial thermal resistance
T	[K]	Temperature
r	[m]	radius

Special characters

α	[W/m²K]	Convective heat transfer coefficient
σ	[W/m^2/K^4]	Stefan-Boltzmann constant
λ	[W/mK]	Thermal conductivity of lime
$\Delta\mathcal{H}$	[J/kg]	Decomposition enthalpy
ε	[-]	Emissivity

Subscripts

F	Furnace
S	Surface of the particle
G	Gas
f	front

Such a minute particles of lime cannot be representative of limestone which undergo decomposition in industrial kilns. So in the current study larger limestone particles have been considered. It was found that thermal conductivity is one of the most influencing parameters of calcination process [6,7]. The present study focuses on determination of the thermal conductivity of product lime. It is the most influencing material property for the decomposition time.

EXPERIMENTAL SETUP

The thermal conductivity of several lime types were determined alternatively with thermogravimetric measurements as shown in Figure 1. In an electrically heated tube furnace, cylindrical samples were calcined at different conditions. The samples were hanging on a balance. In the core of the particle a hole was drilled in which a thermocouple was placed, so that the temporal profile of the weight loss (decomposition) and core temperature could be measured continuously. The samples had a diameter of 20 mm to 35 mm. The length of the particles were four to five times of the diameter. Both face sides were insulated so that the decomposition profile could be considered one-dimensional in the radial direction. The cylinders were decomposed for different furnace temperatures in air or in pure carbon dioxide. The flow velocities and the temperatures of the gases were measured.

1. Chamber furnace
2. Carbonate sample
3. Balance
4. Pump CO2 feed-in
5. CO2 flow meter
6. Pump air feed-in
7. Air flow meter
8. Ceramic packed bed
9. Thermocouple for gas temperature
10. Thermocouple for wall temperature
11. Thermocouple for sample temperature
12. Measured data logger
13. Computer
14. Insulation

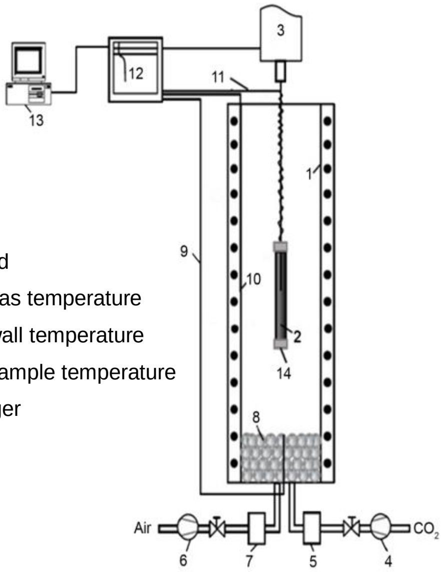

Figure 1: Thermogravimetric furnace to measure calcination behavior

Figure 2 shows the measured temperature (a) and conversion (b) profiles of the two samples K and H respectively. It is an example of the dependence of the core temperature and the decomposition profile on time for the two types of limestones K and H. The furnace temperature is around 1050°C. It can be seen that both types have different decomposition times and characteristic profiles of the core temperature. Initially the core temperature of the particle reaches to the range of decomposition temperature and appears to maintain at this temperature range almost until the end of decomposition. The transient behaviour of the core temperature is observed during the early stage of decomposition and again at the end of decomposition. The decomposition profiles are quasi-stationary in the range of $0.3<X<0.9$. That means that the decomposition front moves to the interior over time, but the heat transfer to the reaction front can be described with the equations for the stationary heat transfer [7, 9, and 10]. It is reasonable because the transferred heat is converted nearly completely into reaction enthalpy. The stored enthalpy is negligible in contrast. The more details about this method is elaborately explained in [7 ,12].

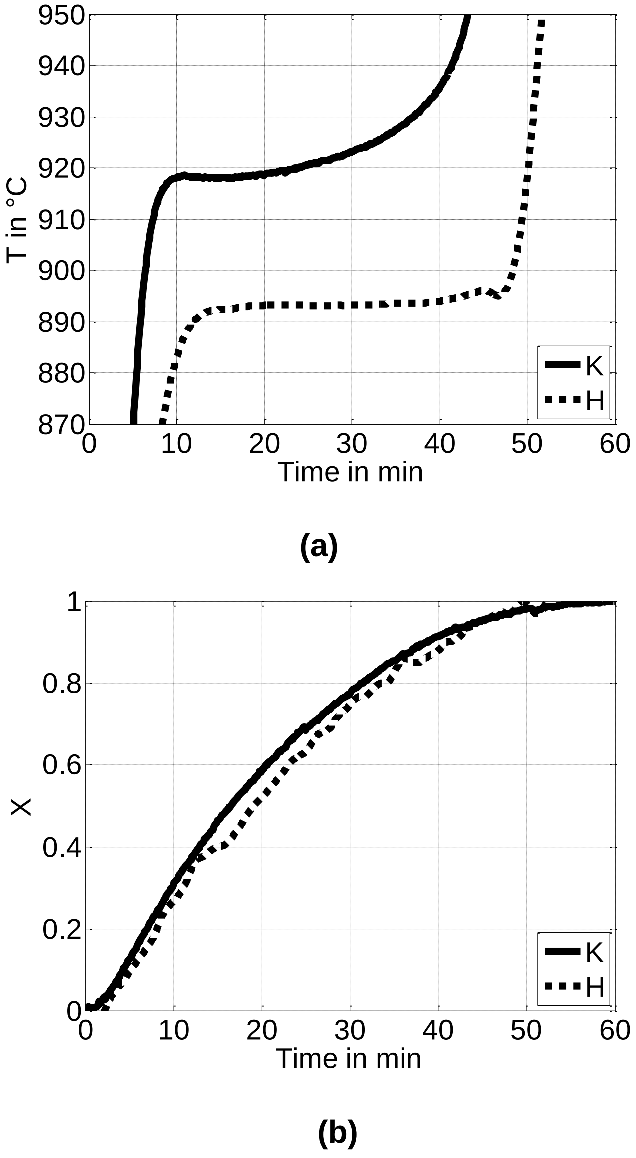

Figure 2 Comparison of the temperature (a) and conversion (b) profiles for two different limestone particles at a constant kiln temperature of 1050 °C

MODEL DESCRIPTION

The wall of the furnace radiates heat to the sample, from which a smaller part of heat is discharged convectively by the gas. The transferred heat flow is calculated with

$$\dot{Q} = \varepsilon_S \cdot \sigma \cdot A_S \cdot \left(T_F^4 - T_S^4\right) - \alpha \cdot A_S \cdot \left(T_S - T_G\right) \tag{2}$$

where ε_S is the emissivity of the sample, σ is the Stefan-Boltzmann constant, A_S is the outer surface of the sample, T_F is the measured wall temperature of the furnace, T_S is the surface temperature of the sample, α is the heat transfer coefficient and T_G is the measured gas temperature. It was measured near to the particle. The emissivity is known from the measurements which were taken from the literature [11]. The heat transfer coefficient was calculated with the measured flow velocity and the known Nusselt functions. The unknown surface temperature of the sample is determined by the condition that the transferred heat flow is conducted through the decomposed lime shell to the reaction front. Therefore,

$$\dot{Q} = \frac{2\pi L\lambda.(T_s - T_f)}{\ln\left(r_s/r_f\right)} \qquad (3)$$

Here, λ is the desired thermal conductivity, r_s is the outer radius of the reaction front, r_f is the radius of the reaction front and T_f is the temperature of the reaction front, which is equal to the core temperature. The subscripts F and f are referred for the Furnace and the reaction front respectively.The radius of the reaction front can be determined with the measured decomposition degree.

$$X=1-\left(r_f/r_s\right)^2 \qquad (4)$$

From this, the following heat flow results

$$\dot{Q} = -K_{CO_2}.\frac{dX}{dt}.\pi r_s^2 L.\Delta H_f \qquad (5)$$

where ΔH_f is the decomposition enthalpy (168 kJ/kmol or $3.82.10^6$ J/kg of CO_2 gas) and dX/dt is the temporal change of the decomposition degree. From the above set of equations, the unknown parameter thermal conductivity has been solved at different conversion degree values. The emissivity values of various lime particles have been measured and reported [11]. However, for the present lime particles it is still unknown. But measurements in [11] gives a possible range of emissivity which is in the range of 0.25 to 0.6.

The dependence of the calculated thermal conductivity of lime layer on the conversion degree for the lime H and lime K is shown in Figures 3 and 4 as an example. The parameter is the emissivity. Its value is not known. The emissivity of every lime investigated is not exactly known. Therefore, a value must be given to the analysis. The calcination at the beginning is dominated by the radiation heat transfer. Therefore, the influence of the emissivity is relatively strong and hence huge variation of conductivity was found in both the Figures 3 and 4 for lower conversion degrees. The end of the calcination is dominated by the heat conduction. Therefore, the emissivity has only a low influence. The emissivity must be the same during the complete decomposition. Hence the emissivity was assumed to be appropriate for determining the thermal conductivity which gives nearly a horizontal profile.

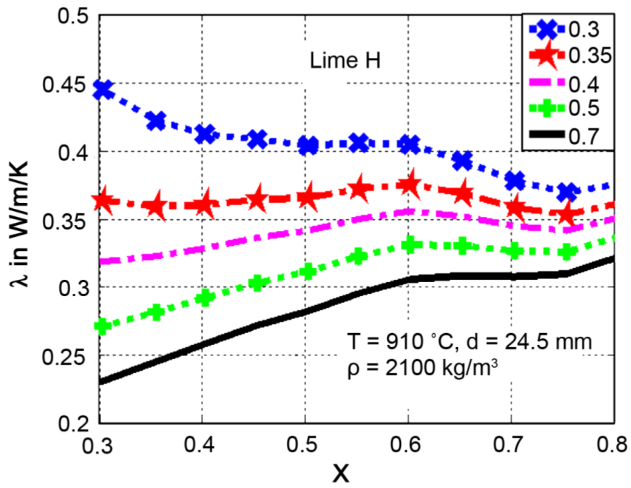

Figure 3: Thermal conductivity determined during the decomposition of lime H versus conversion degree

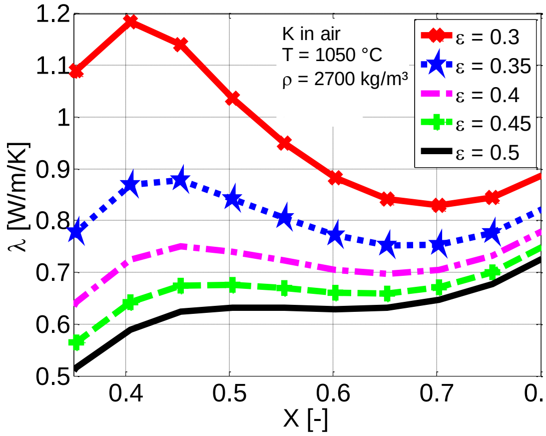

Figure 4: Thermal conductivity determined during the decomposition of lime K versus conversion degree

In Figure 3 the emissivity of 0.35 [11] and the belonging conductivity 0.36 W/mK can be determined. In the Figure 4, for the emissivity of 0.35, the average conductivity 0.85 W/mK can be determined. In both of these Figures, the conductivity corresponds to this emissivity value shows nearly horizontal profile. Using the gravimetric method, the thermal conductivities of several limestones have been determined. They are valid for a mean temperature between the reaction front and the surface.

VALIDATION WITH LASER FLASH ANALYSIS RESULTS

In the literature, very few attempts have been made to study the thermal conductivities of limestone. Silva [7, 12-15] conducted several experiments with a laser-flash apparatus from

NETZSCH (Model: LFA 427). Thermal diffusivities of limestone and lime are measured up to the temperature ranges of 600°C and 1300°C respectively. From the experimental data of the specific heat capacity and thermal diffusivity of limestone and lime of different origins, the thermal conductivities were determined and are plotted in the Figure 5.

In Figure 5, average thermal conductivities for 6 different types of lime are plotted with respect to the temperature. In this figure limes K and M exhibit the highest and lowest thermal conductivities. From this figure it can be noticed that the range of thermal conductivity at the decomposition temperature range 900°C – 1200°C varies between 0.4 – 0.9 W/mK. Lime K which exhibits highest conductivity is the one used in the present study (Figure 4) is shown along with other samples studied in the literature. At 1000°C, Lime K exhibits a conductivity of 0.9 W/mK. The present decomposition method determines the value as 0.85 W/mK as shown in Figure 4. These two methods are differed only by 6%. This difference is acceptable subjected to the possible errors in either of the methods. None of the other limes are in common in both of these two methods and hence cannot be compared.

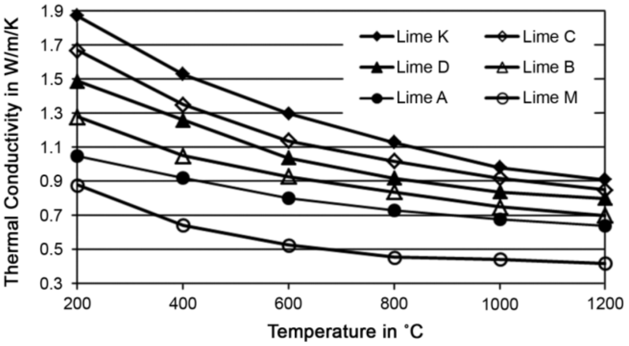

Figure 5: Thermal conductivities of various lime types [12]

IMPORTANT RESULTS

However, as could be seen from the Laser Flash Analysis, the dependency of the conductivity on temperature is very weak in the high temperature range. In Figure 6, all determined conductivities of lime from various limestone are plotted with respect to the bulk density of the respective limestone. The higher this bulk density is the higher is the value of the conductivity. The lower the density the higher must be the porosity.

Hence, a particle porosity ε_p is defined as

$$\varepsilon_p = 1 - \frac{\rho_R}{\rho_S}$$

where ρ_R is the apparent density and ρ_S is the material density of lime. The solid density of lime is 3360 Kg/m³ for lime. From the above Figure 6 (a), it can be said that the lime obtained from limestone with higher density has higher conductivity. This could be because of lower porosity.

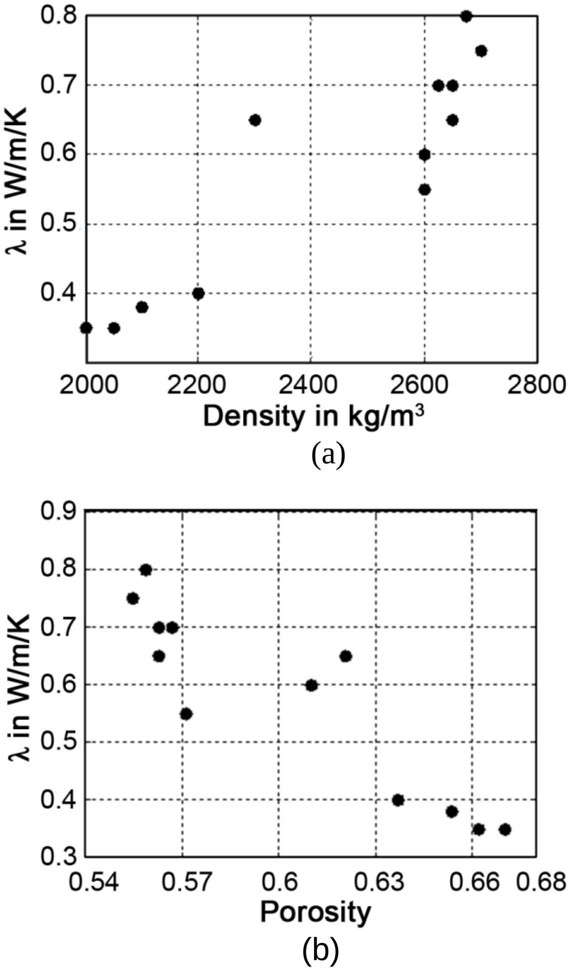

Figure 6: Calculated thermal conductivities of different limes
(a) Variation with respect to limestone density
(b) Variation with respect to porosity

CONCLUSIONS

Thermogravimetric experiments with shrinking core model can be used to determine the thermal conductivities of lime of various limestone samples from different origins. This method is validated with standard Laser Flash Analysis method. The present method is advantageous because the sample used is representative of the stone used in Industry. Higher density stones are found to have higher conductivities. Heavier stones with higher thermal conductivities reach higher core temperatures during initial transient phase of decomposition. These stones decompose at relatively higher temperatures and could result in hard burnt lime as the output.

REFERENCES

[1] W. A. Gilkey, “Calcination Rates of Limestone,” Ind. Eng. Chem., pp. 727–728, 1926.

[2] F. Garcã, A. Abad, L. F. De Diego, P. Gayã, and J. Adã, “Calcination of calcium-based sorbents at pressure in a broad range of CO2 concentrations,” Chem. Eng. Sci., vol. 57, no. 13, pp. 2381–2393, 2002.

[3] J. Khinast, G. F. Krammer, C. Brunner, and G. Staudinger, “Decompostion of Limestone: The influence of CO2 and particle size on the reaction rate,” Chem. Eng. Sci., vol. 51, no. 4, pp. 623–634, 1996.

[4] H. Mikulčić, E. Von Berg, M. Vujanović, P. Priesching, R. Tatschl, and N. Duić, “Numerical Modelling of Calcination Reaction Mechanism,” vol. 3, no. 1, pp. 2–6, 2011.

[5] H. Mikulčić, E. von Berg, M. Vujanović, P. Priesching, L. Perković, R. Tatschl, and N. Duić, “Numerical modelling of calcination reaction mechanism for cement production,” Chem. Eng. Sci., vol. 69, no. 1, pp. 607–615, Feb. 2012.

[6] Sandaka, G.: Calcination behavior of lumpy limestones from different origins. (2016) Dissertation Otto-von-Guericke-Universität Magdeburg.

[7] Silva, M.; Sandaka, G.; Specht, E.; Al-Karawi, J.: Thermophysical properties of lime as a function of origin (Part 4): Conductivity: Cement Lime Gypsum (2017), Issue 3/2017.

[8] Kainer, H.; Specht, E.; Jeschar, R.: Pore diffusion, reaction and thermal conduction coefficients of various limestones and their influence on decomposition time.
Cement, Lime, Gypsum 39 (1986), 5, 259-268 (deutsch). Cement, Lime, Gypsum 39 (1986), 7, 214-219 (englisch).

[9] Cheng, C.; Specht, E.; Kehse, G.: Influence of origin and material property of limestone upon its decomposition behaviour in shaft kilns. Cement, Lime, Gypsum 60 (2007) No. 1, 51-61.

[10] Sandaka, G.; Specht, E.: Modeling and Experiments of Lime Calicination. ECCOMAS Special Interest Conference, Numerical Heat Transfer 2012, 4-6 September 2012, Gliwice-Wroclaw, Poland, 567-573.

[11] Moldenhauer, A.; Bauer, W.; Specht, E.: Thermophysical properties of limestone as a function of origin. Part 3: Emissivity. Cement Lime Gypsum No. 10 (2016).

[12] Silva, M.; Specht, E.; Schmidt, J.: Thermophysical properties of limestone as a function of origin. Part 1: Specific heat capacities. Cement Lime Gypsum No 2 (2010) 55-62.

[13] Silva, M.; Specht, E.; Schmidt, J.: Thermophysical properties of limestone as a function of origin. Part 2: Calcination enthalpy and equilibrium temperature. Cement Lime Gypsum Int. (2010) No 6, 51-57.

[14] Silva, M.; Specht, E.; Schmidt, J.; Al-Karawi, J.: Influence of the origin of limestone on its decomposition temperature and on the specific heat capacity and conductivity of lime. High Temperature-High Pressure 38 (2010), 361-378.

[15] Silva, M.: Experimental investigation of the thermophysical properties of new and representative materials from room temperature up to 1300 °C. (2009) Dissertation Otto-von-Guericke-Universität Magdeburg.

[16] Kainer, H.; Specht, E.; Jeschar, R.: Pore diffusion, reaction and thermal conduction coefficients of various limestones and their influence on decomposition time.
Cement, Lime, Gypsum 39 (1986), 5, 259-268 (deutsch).
Cement, Lime, Gypsum 39 (1986), 7, 214-219 (englisch).

[17] Cheng, C.; Specht, E.; Kehse, G.: Influence of origin and material property of limestone upon its decomposition behaviour in shaft kilns. Cement, Lime, Gypsum 60 (2007) No. 1, 51-61.

[18] Specht, E.: Wärme- und Stoffübertragung in der Thermoprozesstechnik. Vulkan-Verlag, 2014.

[19] Parker, W.J.; Jenkins, R.J.; Butler, C.P.; Abbott, G.L. J Appl. Phys.: A Flash Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity, Vol. 32, 1679 (1961).

[20] Vozár, L.; Hohenauer, W.: Flash method of measuring the thermal diffusivity. A Review. High Temp-High Press 35/36 (2004) 253-264.