



Unit thermal decomposition time of limestone vs. limestone origin and dimensions of cylindrical samples undergoing calcination

Jednostkowy czas rozkładu termicznego kamienia wapiennego w funkcji jego pochodzenia i rozmiaru kalcynowanych próbek cylindrycznych

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ABSTRACT

With today's requirements for increased productivity imposed by all customers, a good understanding of the limestone calcination process is very important. There are several process variables that are crucial in optimization of the limestone calcination. This paper is addressing the impact of a size of the calcined pieces, and a quality of the limestone (purity and homogeneity) on the unit thermal decomposition time. It is shown that the thermal decomposition rate of various limestones is statistically different depending on the limestone origin, affecting heterogeneity of physicochemical properties of heated samples, and their dimensions. A decrease of unit thermal decomposition time values, scaled with the unit initial sample mass, with increased dimension of a cylindrical sample placed in a cylindrical heating chamber with constant dimensions is also documented in the paper. Moreover, the coefficient of variation of the unit thermal decomposition time of the limestone samples depends on the properties of calcined limestone and the conditions of calcination determined first of all by radiation heat transfer between heating chamber walls and the sample surface, and secondly by carbon dioxide transport from the reaction surface to the heating chamber filled with a gaseous mixture.

KEYWORDS: Limestone, Thermal decomposition, Lime, Calcined sample dimension

STRESZCZENIE

W kontekście obecnych wymagań zwiększonej produktywności narzuconej przez klientów bardzo ważne jest dobre zrozumienie procesu kalcynacji wapienia. Jest kilka zmiennych procesu, które są kluczowe dla optymalizacji kalcynacji wapienia. Artykuł niniejszy odnosi się do wpływu rozmiaru kalcynowanych kawałków i jakości wapienia (czystość i jednorodność) na jednostkowy czas rozkładu termicznego. Pokazano, że szybkość rozkładu termicznego różnych wapieni jest statystycznie różna zależnie od pochodzenia wapienia, które oddziałuje na jednorodność właściwości fizykochemicznych ogrzewanych próbek, a także od ich wymiarów. Udokumentowano spadek wartości jednostkowego czasu rozkładu termicznego, liczonego na jednostkę masy, wraz ze wzrostem wymiaru cylindrycznej próbki umieszczonej w cylindrycznej komorze ogrzewania o stałych rozmiarach. Poza tym współczynnik zmienności jednostkowego czasu rozkładu próbek wapienia zależy od jego właściwości i warunków kalcynacji, określonych przede wszystkim przez przekazywanie ciepła drogą promieniowania pomiędzy ścianami komory ogrzewania i powierzchnią próbki, a także przez transport dwutlenku węgla od powierzchni reakcji do komory ogrzewania wypełnionej gazową mieszaniną.

SŁOWA KLUCZOWE: wapień, rozkład termiczny, wapno, rozmiar kalcynowanej próbki

1. Introduction

Calcination of limestones is an important industrial process utilized for production of lime which is the basic product of chemical industry. Simplicity of thermal decomposition of various types of limestones is only apparent. The following factors influence thermal decomposition of limestones in industrial conditions:

- carbon dioxide content in a gaseous mixture which surrounds calcined limestone grains and slows down the chemical reaction rate; the equations describing the phenomenon are constantly not known,
- dimension of calcined limestone grains which affects the conditions of heat and mass transfer inside the calcined limestone grain,
- content of contaminants influencing the thermal decomposition reaction rate [1],
- heterogeneity of physicochemical properties of limestone, being the natural, sedimentary rock [2].

There are only a few works referring to the thermal decomposition of big limestone grains (lumps). The texture of carbon dioxide flow ways in a created layer of lime basically influences the calcination rate of big grains [3], e.g. in the most modern Maerz parallel flow regenerative kilns used for lime production, the sizes of stone pieces are various, e.g. 30–120 mm and 15–40 mm, and depend on the type of furnace [4]. A new method of loading of limestone is used at present. The method relies upon the alternate arrangement of furnace charge layers with the coarse charge and fine one. The method improves both the produced lime quality and working parameters of the furnace, including a decrease of pressure of gaseous mixture which flows through the grain furnace charge [4].

The impact of the origin and size of big limestone cylindrical samples on the unit thermal decomposition time of three limestones is analysed in this paper, using statistical tools. The Shapiro-Wilk test of normality was used together with the *P*-value (observed significance level), single factor analysis of variance (ANOVA) and the Bennett test for homogeneity of coefficients of variation of investigated properties. The samples were taken from the Polish Jurassic, Precambrian and Triassic limestone deposits [5, 6]. The homogeneity of coefficients of variation of the unit thermal decomposition time was determined in order to check normality of coefficients of variation distribution. Moreover, the impact of geometric arrangement of the heated sample – heating chamber system on the unit thermal decomposition time was investigated. The point is that the configuration factor well-known from the radiation heat transfer principles changes when a size of heated sample changes in respect to a chamber of constant size.

The obtained results within the above indicated scope of investigations widen the knowledge referring to the process and they may be used for the modelling of thermal decomposition of limestone grain layer of the furnace charge.

2. Experimental procedure

Cylindrical samples of diameters ranging from 48 mm to 95 mm and a ratio between diameter and height close to 1 were used in the study. The investigations were performed by using the Jurassic limestone from the Morawica deposit, the Precambrian limestone from the Stronie Śląskie deposit and the Triassic limestone from the Tarnów Opolski deposit. The above mentioned deposits are located in Poland. The physicochemical properties and microfabrics of the limestones are described in Refs. [5] and [6].

8 samples of each investigated limestone were calcined in a heating chamber of a vertical electric furnace [7] equipped with a thermobalance and a preheater. An internal dimension of the heating chamber was 120 mm. A mixture of air and 45.16 vol.% of carbon dioxide was supplied to the heating chamber. The carbon dioxide is an important absorbing-emitting agent which affects heat transfer and heat balance of the calcination process. The temperature of the preheated gaseous mixture in the heating chamber inlet was about 450 °C. The samples were heated with a heating ratio of about 3.7 °C min⁻¹ up to a temperature of about 1050 °C of the outer wall of the heating chamber and further the temperature was kept constant up to receiving a constant weight by the samples. A time needed for full decomposition of the limestone samples was measured and related to the initial sample mass to determine the unit thermal decomposition time expressed in s·g⁻¹.

In analysis of both experimental data, the Shapiro-Wilk test of normality was used together with the *P*-value, single factor analysis of variance (ANOVA) and the Bennett test for homogeneity of coefficients of variation of investigated properties.

Kinetics of thermal decomposition of very fine limestone grains with dimension up to several micrometers is described in a lot of papers. The concise review of the topic is included in Ref. [1]. However a few works are devoted to the modelling of thermal decomposition of limestone big grains (lumps). The flow of carbon dioxide from the reaction surface to the environment of calcined grain through a produced lime layer essentially influences the calcination rate [3] due to the texture of the lime layer.

3. Results and discussion

3.1. Impact of limestone origin on unit thermal decomposition time of cylindrical limestone samples

The results of thermal decomposition time of the studied cylindrical limestone samples with diameters being close to 48 mm are shown in Table 1. Expanded uncertainties are calculated according to the method shown in the guide to the expression of uncertainty in measurements [8] assuming the value of the coverage factor k equal to 2. Therefore, the intervals of the unit thermal decomposition time having a level of confidence of approximately 95 percent are $63.71 \text{ s} \pm 1.78 \text{ s}$, $51.09 \text{ s} \pm 1.27 \text{ s}$ and $55.09 \text{ s} \pm 1.77 \text{ s}$ for the Jurassic, Precambrian and Triassic limestone, respectively.

The Shapiro-Wilk test [9, 10, 11] was used for determination of normality of each single sample of independent observations of the unit thermal decomposition

time shown in Table 1 for each investigated limestone. The alternative conclusions were: (i) H_0 : a random sample τ_{ik} comes from a normal distribution, (ii) H_1 : a random sample τ_{ik} does not come from a normal distribution.

The computation results of the Shapiro-Wilk test statistic W and the P -value are shown in Table 2. The Shapiro-Wilk test is the left tailed one, therefore the conclusion H_0 is accepted, because W calculated was higher than $W_{crit} = 0.818$ at $\alpha = 0.05$ and $N = 8$. It means that the samples of the unit thermal decomposition time come from the normal distribution.

To make sure that statistically significant differences exist between the unit thermal decomposition times for the studied limestones shown in Table 1, the single factor ANOVA was performed. The calculation results of the single factor ANOVA study are shown in Table 3. The alternatives are: (i) H_0 : $\tau_1 = \tau_2 = \tau_3$ (index 1, 2, and 3 means the sample of the Jurassic, Precambrian and Triassic limestone, respectively), (ii) H_1 : not all τ_i are equal.

Table 1. Unit thermal decomposition time of studied limestone samples.

Limestone	Jurassic	Precambrian	Triassic
Dimension of samples D [mm]	47.72 ± 0.12	48.51 ± 0.11	47.86 ± 0.22
Dimension to height ratio D/H [-]	0.931 ± 0.015	0.974 ± 0.019	0.999 ± 0.024
Surface area per unit mass of sample A [$\text{cm}^2 \cdot \text{g}^{-1}$]	0.516 ± 0.006	0.464 ± 0.007	0.563 ± 0.014
Run no. N_{ik}	Unit thermal decomposition time τ_{ik} [$\text{s} \cdot \text{g}^{-1}$]		
1	61.10	49.24	56.35
2	64.93	49.63	58.57
3	62.82	51.76	55.01
4	68.17	50.47	55.84
5	59.96	50.95	54.17
6	64.07	49.41	51.74
7	63.72	53.05	51.59
8	64.89	54.19	57.45
Mean value \bar{X}	63.709	51.086	55.090
Standard deviation s	2.52	1.80	2.51
Coefficient of variation CV_i^*	0.040	0.035	0.046

* Coefficient of variation is calculated according to equation: $CV_i = s/\bar{X}$.

Table 2. Calculation results of W – statistic for unit thermal decomposition time of the samples shown in Table 1.

Limestone	Jurassic	Precambrian	Triassic
Dimension of samples D [mm]	47.72 ± 0.12	48.51 ± 0.11	47.86 ± 0.22
W	0.9659	0.9114	0.9445
P -value	0.8642	0.3638	0.6562
W_{crit} ($\alpha = 0.05, N = 8$)	0.818	0.818	0.818
Conclusion:	accepted H_0	accepted H_0	accepted H_0

Table 3. ANOVA of unit thermal decomposition time of Jurassic, Precambrian and Triassic limestone samples shown in Table 1.

Source of variation	Sum of squares	df	Mean square	F	$F_{0.05;2,21}$
Total	777.14	23			
Treatments (type of limestone)	665.74	2	332.87	62.75	3.47
Error	111.40	21	5.30		

The computed F test statistic is $F = 62.75 > F_{crit} = F_{0.05;2,21} = 3.47$, therefore the calculated F value falls in the rejection region and H_1 is concluded. The result of the analysis shows that there are statistically significant differences between the unit thermal decomposition times for the studied limestones.

Moreover, homogeneity of coefficients of variation (CV) shown in Table 1 was analysed. The analysis was performed with the aid of the Bennett test [12]. The alternatives were: (i) $H_0: CV_1 = CV_2 = CV_3$ (CV_i – coefficient of variation in population), (ii) $H_1: CV_1 \neq CV_2 \neq CV_3$.

The calculated Bennett test statistic is $Z = 6.203 > \chi^2_{0.05;2,21} = 5.991$. Therefore, the calculated Z value falls in the rejection region and H_1 is concluded. It means that the coefficients of variation of unit thermal decomposition time of the studied limestones show statistically significant differences.

Differences in unit thermal decomposition times and heterogeneity of coefficients of variation of unit thermal decomposition times of the limestones are the result of differences of physicochemical properties of the limestones, which are natural sedimentary rocks, as well as the calcination conditions of a sample.

3.2. Impact of size on unit thermal dissociation time of limestones cylindrical samples

The unit thermal decomposition time of a limestone cylindrical sample placed in a cylindrical heating chamber depends also on the sample dimensions. Let us suppose that the sample with a diameter D_1 is heated in the cylindrical heating chamber with the same heating curve as in case of the sample with a diameter D_2 as it is shown in Fig. 1. Moreover, it is assumed that the composition of gaseous mixture supplied to the heating chamber is the same in both cases. The unit thermal decomposition times of both these samples differ between each other due to the various values of radiation heat fluxes transmitted to each sample undergoing thermal decomposition. Radiation is the fundamental mechanism of heat transmission between the sample surface and the heating chamber wall surface in calcination temperature interval. Convection does not play so important role in the heat transfer in the considered temperature interval of the two surfaces. The radiation heat flux transferred between the outer sample surface and the inner heating chamber one, $Q_{1,2}$, depends on the surface area of the sample, F_1 , according to the formula [13]:

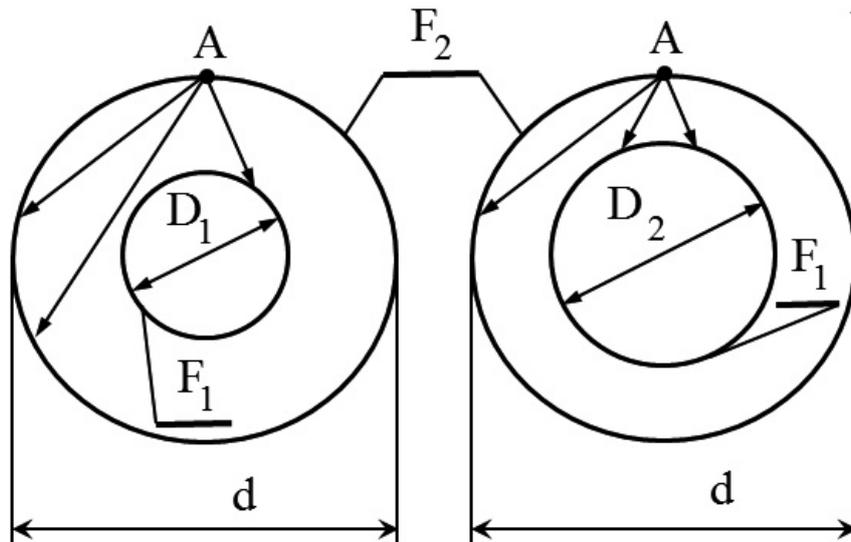


Fig. 1. Cylindrical samples of calcined limestones centrally placed in heating chamber and $D_1 < D_2$, and F_1 is outer calcined sample surface, but F_2 is the heating chamber surface.

Table 4. Unit thermal decomposition time of the Triassic limestone samples with various dimensions.

Dimension of sample D [mm]	47.86 ± 0.22	72.96 ± 0.14	95.41 ± 1.04
Dimension to height ratio D/H [-]	0.999 ± 0.024	1.034 ± 0.012	0.969 ± 0.016
Surface area per unit mass of sample A [$\text{cm}^2 \cdot \text{g}^{-1}$]	0.563 ± 0.014	0.361 ± 0.003	0.275 ± 0.007
Run no. N_{ij}	Unit thermal decomposition time τ_{ik} [$\text{s} \cdot \text{g}^{-1}$]		
1	56.3	26.5	16.1
2	58.6	25.0	16.9
3	55.0	26.2	14.7
4	55.8	24.6	14.1
5	54.2	28.9	21.9
6	51.7	27.6	21.3
7	51.6	27.6	17.8
8	57.5	25.0	21.3
Mean value \bar{X}	55.09	26.42	18.02
Standard deviation s	2.5	1.5	3.1
Coefficient of variation CV_i	0.046	0.058	0.173

$$\dot{Q}_{1,2} = \frac{F_1 \sigma}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1} (T_1^4 - T_2^4) \quad (1)$$

where: $\sigma = 5.6703 \cdot 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ is the Stefan-Boltzmann constant, T_1 and T_2 are the temperatures of the sample and heating chamber surfaces, respectively, ε_1 and ε_2 are the relevant coefficients of emissivity. Formula (1) describes the radiation heat transfer schematically shown in Fig. 1. As it is seen, a part of radiation which leaves the surface F_2 in the point A falls on the surface F_2 . The part of the radiation decreases with the increase of the sample diameter. Therefore, the heat flux transmitted by radiation from the chamber wall to the sample is bigger for the bigger diameter sample. Moreover, the surface heterogeneity of the samples may affect the values of the sample surface emissivity, which is included in the formula (1).

The above mentioned description of heat transfer during calcination of limestone sample is simplified. Heat transmission is more complicated in the considered case due to effects of the increased concentration of carbon dioxide, which is evolved during calcination and takes part in radiation heat transfer. The carbon dioxide concentration is bigger and bigger, if the sample dimensions increase. Changes in the carbon dioxide concentration in the gaseous mixture flowing around the sample should be taken into account in the case of more detailed calculations of heat transfer during the limestone grain charge calcination.

The Shapiro-Wilk test was used again for the investigation of normality of the unit thermal decomposition time independent observations. The results show that the samples of unit thermal decomposition time come from the normal distribution again. The single factor ANOVA of unit thermal decomposition times was not performed in this case, because the various sample dimensions were the main reason of differences detected among them.

Homogeneity of coefficients of variation shown in Table 4 was analysed again by using the Bennett test [12]. The test shows heterogeneity of CV coefficients of the unit thermal decomposition time. The coefficient of variation for the samples with the greatest dimensions is one order of magnitude bigger in comparison with the CV value for smaller samples. Therefore, the impact of radiation heat transfer between the sample

and heating chamber surfaces, being separated by an emitting-absorbing gaseous mixture which contain carbon dioxide, on a value of the coefficient of variation is observed.

4. Conclusions

The measured values of the unit thermal decomposition time of geometrically identical samples of the studied limestones show statistically significant differences depending on the origin of limestone which is connected with physicochemical properties of the limestone. It is especially seen in the case of the Precambrian limestone samples. The ratio of sample surface area to its mass was the smallest one and the thermal decomposition time value was the smallest in comparison with other limestones. This was caused by cracking calcite big grains during calcination due to crystallographic anisotropy of linear thermal expansion coefficient of the calcite. This phenomenon is the reason of the formation of fast diffusion ways for carbon dioxide in the lime layer surrounding an unreacted core of the calcined limestone grain.

The dimensions of heated limestone samples and the sample surface heterogeneity influence the unit thermal decomposition time. A decrease of unit thermal decomposition time is observed with increase of the sample dimensions, when the samples are calcined in the heating chamber with constant dimensions. It is a result of bigger and bigger interception of the radiation flux by the sample with bigger dimension.

It is concluded that the value of the CV coefficient of thermal decomposition time indicates can be applied to assess the susceptibility of a limestone charge composed of grains of various dimensions on the homogeneity of thermal decomposition.

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