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On the kinetics of pozzolanic reaction in metakaolin–lime–water system

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Abstract The kinetics of pozzolanic reaction metakaolin–lime is studied in the present work. Metakaolin is prepared by calcination of enriched kaolin (deposit "Senovo", Bulgaria) at temperature of 830 ± 10 °C in a lab-scale muffle oven. The reaction is performed in intensively stirred water suspension at different temperatures in the range 20–100 °C. The kinetics is analyzed by comparing the experimental data with theoretical curves, derived according to appropriate kinetic and diffusion models taking into account the grain size distribution of metakaolin. The macroscopic mechanism and activation energy of the reaction are determined. It is found, that the activation energy decreases gradually from 71 to 45 kJ/mol[$Ca(OH)_2$] with the increase of the reaction degree from 0.2 up to 0.6, respectively, which is a characteristic for transition regime reactions.

Keywords Pozzolanic reaction · Kinetics · Metakaolin–lime reaction · Diffusion

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Introduction

The investigation of the kinetics of pozzolanic reactions is an important experimental task that gives characteristic constants for the reaction rate. Using them, one can evaluate the effectiveness of applying different type of pozzolanic materials as additives to mortars and concretes, as well as to compare their properties.

Most studies on the kinetics of metakaolin–lime interaction have been carried out under conditions, which are modeling the practical use of metakaolin [1–7]. For this purpose, pastes of cement–metakaolin–water or of metakaolin–lime–water are prepared and cured under definite conditions, under which the metakaolin binds the lime to form cement products. Various changes of the rate and mechanism of the hydration process are possible due to the complex character of these systems and depending on the conditions of sample preparation and curing.

In order to diminish the influence of similar factors on the reaction rate, we use a simple experimental model when studying the kinetics of pozzolanic reaction in another complex system kaolin–lime–water [8]. The kinetic analysis is performed by joint presentation of theoretical and experimental data in dimensionless coordinates having in mind the influence of particle size distribution on the reaction rate. This approach is accepted in the present work to establish the kinetic regularities of the interaction metakaolin–lime in water medium.

Experimental

Materials and methods

Starting materials for this study are freshly precipitated calcium hydroxide and metakaolin (MK), prepared from enriched kaolin (deposit “Senovo”, Bulgaria). The analysis, described in Ref. [8], gives the quantitative chemical composition of the kaolin (in mass%): SiO_2: 53.20, Al_2O_3: 32.63, Fe_2O_3: 0.73, TiO_2: 0.25, CaO: 0.27, MgO: 0.23, K_2O: 1.21, Na_2O: 0.12, losses of ignition (LOI): 11.28. It is found that the enriched kaoline contains 75% kaolinite, 13% quartz, and 10% illite. The rest of mineral components, which include the remaining chemical admixtures in the kaolin, are in insignificant quantity with their sum amounting to about 2%. Table 1 (row 1) gives the grain size distribution data of kaolin, derived by dispersion techniques on a Shimadzu apparatus for grains over 3 μm, and statistically on a SEM Philips 515, for the fraction below 3 μm.

Metakaolin is prepared in a laboratory muffle oven in powder form via calcination of approx. 100 g samples of kaolin, placing them in quartz vessels with a layer thickness of about 2 cm. The optimal conditions for thermal decomposition of kaolin, established experimentally, are: temperature 830 ± 10 °C, duration of the thermal treatment 20 min and cooling down the product in air medium.

The experiments on the kinetic study of pozzolanic reaction metakaolin–lime are carried out in Erlenmeyer plastic flask equipped with reflux condenser, at a ratio of 0.5 g $Ca(OH)_2$:0.5 g MK in 150 ml distilled water. The suspension is stirred with a speed of 200 rpm. It is established that under these hydrodynamic conditions the rate of pozzolanic reaction does not depend on the rate of diffusion in the liquid phase, and therefore, it is a function only of the processes, occurring in the layer of gel-like products, deposited on the surface of pozzolanic particles and/or function of the rate of chemical reaction between these particles and the lime.

Results and discussion

Characterization of the pozzolanic properties of MK

The basic characteristics, determining the pozzolanic properties of metakaolin, are the granulometric composition, LOI, the specific surface area, the content of active phases, and the pozzolanic activity (PA).

The MK samples, used for this study, are characterized by LOI within the range of 0.35–0.5%. At such values, the product meets the requirements for minimal content of not decomposed kaolinite in it and for minimal advancement of secondary reactions, leading to the conversion of MK into a chemically inactive phase with a spinel structure [9, 10].

From the three main mineral ingredients of initial kaolin, quartz practically does not participate in the pozzolanic reaction [8]. The illite component is not completely decomposed during the thermal treatment of kaolin to MK, but it reacts with lime and in this way takes a part to the formation of mechanical strength of the product [11–13]. The illite clays stabilized with lime, however, possess poorer physico-mechanical properties than that of kaolinite. So, the main contribution to the pozzolanic properties of MK should be expected to come from the kaolinite component of enriched kaolin.

The granulometric composition of MK powder (row 2 of Table 1) is derived in the same way as for kaolin. Comparing these data with the particle size of initial kaolin (row 1), it is seen that an aggregation of the particles occurs during the calcination of kaolin and the product should be grinded or disintegrated in order to meet the requirements for its use as pozzolan [9, 14].

The cooled down MK powder is grinded further in a Fritsch planetary mill with agate grinding bodies having diameter of 20 mm at a different duration (the respective results are given in rows 3–6 of Table 1). A decrease in the particle size of material is observed in the case of grinding time interval of 15 min. At a longer grinding duration, however, there is a reverse process—the particle size is growing up with the time interval increasing.

The PA of non-grinded and grinded MK is determined on the basis of Chapelle test [15]. The results from these analyses and the BET specific surface area are plotted in Fig. 1, whereupon the values for PA are the mean of three results for each data point.

Table 1 Granulometric composition of initial kaolin, non-grinded, and grinded MK samples

Sample		Percentage of grains lower than, μm														
		0.5	1	2	3	4	5	6	8	10	20	30	40	50	60	80
Kaolin	1	28	46	62	72	79	83	87	92	95	99	100	–	–	–	–
MK																
Non-grinded	2	–	–	–	7	10	12	15	22	27	43	51	59	63	77	100
15 min	3	–	15	27.5	36	44	50	53	59	72	84	97	98	100	–	–
1 h	4	–	–	–	35	42	48	52	58	63	79	81	86	98	100	–
2 h	5	–	–	–	31	34	37	39	43	46	59	75	82	86	95	98
5 h	6	–	–	–	1	1	1	2	3	5	30	54	59	80	94	98

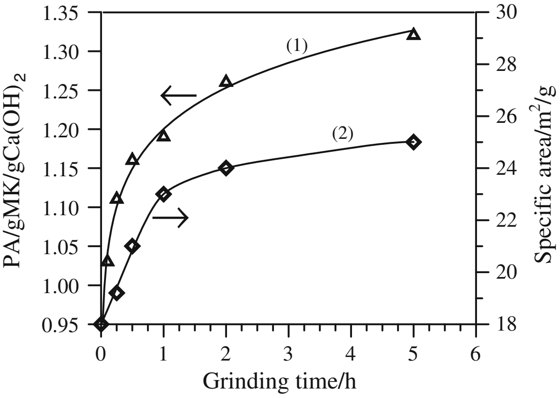

Fig. 1 PA (*1*) and specific surface area (*2*) of the initial and grinded MK

On the basis of data listed in Table 1 and plotted in Fig. 1, one can see that the specific surface area is growing up slowly in the course of grinding time and this growth is proportional to PA. Taking this into account, one can conclude that the observed aggregation of particles in the case of longer grinding time intervals is due to the specific physical–mechanical properties of MK, which is a soft material and its particles are smashed on the surface of grinding bodies in the mill. In the course of this process, there is also a formation of weakly bound aggregates due to the secondary aggregation in parallel to revealing of new reaction surface.

From the data given in Table 1 and Fig. 1, one can conclude that a time interval of 15 min grinding is enough to obtain MK characterized by an appropriate grain size distribution [9], specific surface area of about 19 m^2/g and PA of about 1.1 g [$Ca(OH)_2$]/g [MK]. These results for PA are nearly 25% lower than those for highly reactive metakaolin (HRM), binding up to 1.6 g [$Ca(OH)_2$]/g [HRM] [14]. This difference is probably due to the mineral composition of the initial raw materials, which consists of about 90–95% kaolinite in the case of HRM, while our starting kaolin posses of 75% kaolinite.

The product of pozzolanic reaction between MK, grinded within 5 h, and lime is studied by scanning electron microscope. Only the presence of quartz particles is registered, while MK particles are not established in the reaction product. This shows that the reaction is finished at values for PA of about 1.3 g [$Ca(OH)_2$]/g [MK] (see Fig. 1).

The MK, obtained at the specified above optimal conditions and grinded for 15 min, is used further in the kinetic study of pozzolanic reaction.

Temperature dependence of the reaction rate

The experiments on the kinetics of MK–lime reaction are carried out at constant temperatures of 20, 35, 55, 70, and 100 °C, maintained with an accuracy of ±1 °C and duration of up to 7 days (168 h). The experimental conditions ensure constancy of the lime reactant concentration into the solution as the reaction proceeds. The temperature 20 °C is characteristic for the conditions, under which MK reacts with lime during the stabilization of soil materials, while the temperature 35 °C is close to the maximal one, which occurs in mortars and concretes by MK addition [16]. Taking into account the experimentally established fact that the pozzolanic reaction is completed at values of about 1.3 g [$Ca(OH)_2$]/g [MK], the data of PA are recalculated as the degree of conversion, α, by dividing them by this value. The results for α versus time are plotted in Fig. 2.

The obtaining of kinetic constants of clear physical meaning, regarding the pozzolanic reaction metakaolin–lime, depends on the adequacy of the model, applied to analyze the experimental data. The Jander equation, used for this purpose in [2–4], is not suitable for our case due to the following reasons:

- the size of metakaolin particles vary in a wide interval, see Table 1, and their distribution influence

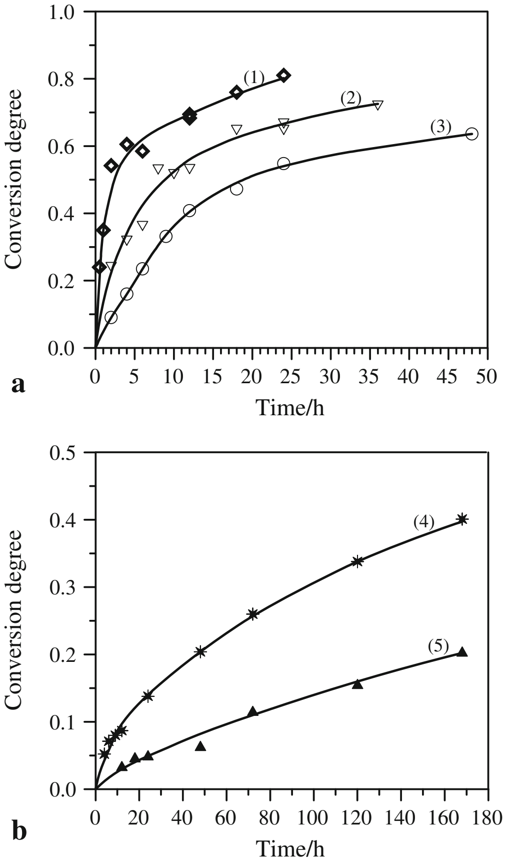

Fig. 2 Conversion degree versus time at temperatures over 50 °C (**a**) and below 40 °C (**b**). Legend: (*1*) 100 °C (*diamond*); (*2*) 70 °C (*downturned triangle*); (*3*) 55 °C (*circle*); (*4*) 35 °C (*star*); (*5*) 20 °C (*filled triangle*)

considerable the kinetics of the pozzolanic reaction and should be taken into account;

- the satisfactory application of Jander equation, derived for mixtures consisting of equal in size and spherical in form powder particles, is possible at relative low reaction degree—up to 0.30 ÷ 0.35 [17];

Frias et al. [18] reported the rate constant of pozzolanic reaction in the sugarcane straw-clay ash/lime system in water at 40 °C determined by the use of a kinetic-diffusive model, suggested by Villar-Ciciña [19]. Based on the correlation between the theoretical model and experimental data, the authors have drawn the conclusion, that the chemical interaction on the particles surface is the rate controlling step.

The experimental data in the present work are imposed on theoretical curves, derived on the basis of suitable kinetics and diffusion models in dimensionless coordinates. In account of the amorphous character of MK, it is assumed that the reaction occurs isotropically and the unconverted kernels of particles reduce their size homotetically with the time, i.e., the shape and relative size of particles will not affect sufficiently the kinetics of process.

The kinetic equations, which describe the chemical interaction and diffusion process in the system polydisperse solid material–liquid/gaseous phase, are solved by integrating expressions, which include the auxiliary functions $\alpha(r_0,t)$ and $M(r_0)$ [20, 21]. The method of determination of the function $\alpha(r_0,t)$ is described in [8]. The differential granulometric curve in Fig. 3 is used to specify the function $M(r_0)$, where we assume that the upper limit of calcined kaolinite grains is represented by the dashed line.

The calculations of $\alpha(r_0,t)$ and the determination of respective values of $M(r_0)$, enable the computation of theoretical curves for the chemical and for the diffusion process.

The calculated theoretical curves are represented in Fig. 4a and b in dimensionless conversion degree–time, where t stands for the real time, while $t_{0.4}$ and $t_{0.5}$ are the times needed to reach α equal to 0.4 and 0.5, respectively. Superimposed on them in the same coordinates are the results from Fig. 2. It is seen in Fig. 4 that the experimental data are located near the theoretical curve for a diffusion process, which is an indication for the rate-limiting effect of diffusion on the total reaction rate.

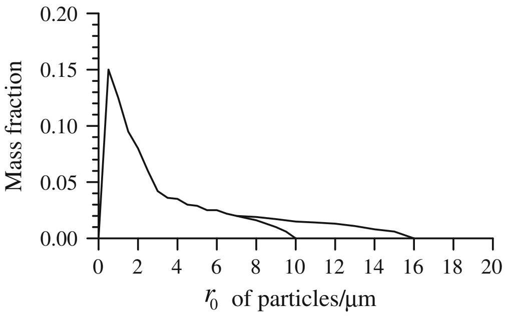

Fig. 3 Differential size distribution curve of MK particles (15 min grinding time)

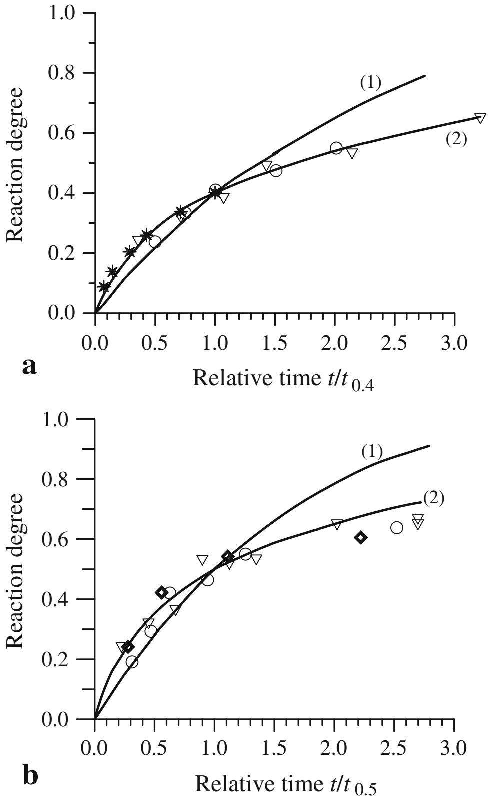

Fig. 4 Experimental data and theoretical curves in dimensionless coordinates versus time for $t/t_{0.4}$ (**a**) and $t/t_{0.5}$ (**b**). Legend: (*1*) chemical reaction curve; (*2*) diffusion curve; *diamond* 100 °C; *downturned triangel* 70 °C; *circle* 55 °C; *star* 35 °C; *filled triangle* 20 °C

Activation energy determination

The activation energy of pozzolanic reaction MK–lime is determined by plotting of iso-α-intersecting lines on the kinetic curves in Fig. 2 and estimating of the time interval t_i for reaching the as-selected values for $\alpha_i = 0.2$, $\alpha_i = 0.5$, and $\alpha_i = 0.6$. The values of activation energy are calculated from the slope of linear dependences, which are obtained in coordinates ln t_i and the reciprocal value of temperature, $1/T$ in K^{-1}. It is seen from Fig. 5, that with the increase of reaction degree α_i, the activation energy, E_a, gradually decreases from 71 kJ/mol $Ca(OH)_2$ at $\alpha_i = 0.2$ down to 45 kJ/mol $Ca(OH)_2$ at $\alpha_i = 0.6$.

The results obtained for the activation energy show that, under the chosen conditions, both—the diffusion rate of $Ca(OH)_2$ species (molecules, ions) inside the gel layer and the chemical reaction rate affect the total rate of pozzolanic

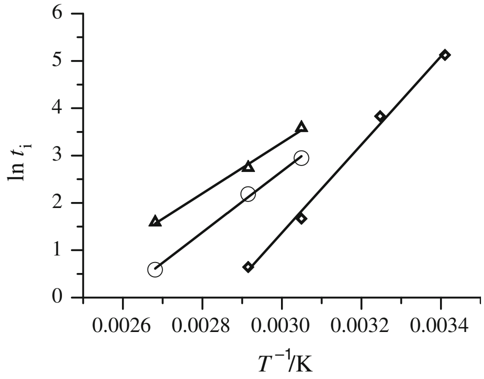

Fig. 5 Logarithm of the time to reach reaction degrees 0.2, 0.5, and 0.6 versus reciprocal value of temperature: 0.2 *diamond*; 0.5 *circle*; 0.6 *triangle*

reaction. From the decrease in activation energy with the advance of reaction in the depth of particles, it follows that the effect of diffusion upon the total rate is increasing. The as-outlined mechanism of the process is characteristic for the initial stages of reaction MK–lime, when there is a high content of water in the gel layer. Other chemical reactions can occur in parallel with the chemical interaction on the reaction phase boundary, such as formation of crystalline hydrates in the gel layer, whereupon lime is consumed by all of them. The slower rate of crystalline hydrate formation, compared to the growing gel layer, however, shows that the rate of chemical interaction on the reaction phase boundary affects the total rate, but not the rate of crystalline hydrates formation.

One can use different methods to estimate numerically the rate constants in certain temperature interval applying the method in dimensionless coordinates, when the total rate of process is limited by the rate of chemical reaction [20], or when the total rate is limited by the diffusion [21]. However, these methods are inapplicable to the case, considered here, when the process occurs in the transition region and the macroscopic mechanism of total reaction is changing with the increase of reaction degree.

Some of the experimental data obtained in the present work and in the work of Frias [19], are similar. For example, the degree of fixed $Ca(OH)_2$ at 40 °C for 7 day curing period is 57%, whereas by our experiments for the same curing period at 35 °C is 34%. The difference is probably due to the higher pozzolanic activity and specific properties of the sugarcane straw-clay ash material, in comparison with our metakaolin.

The experimental data, given in Fig. 2, and the results from the kinetic analysis of the pozzolanic reaction MK–lime obtained in this work can be used to achieve high rates and high degrees of interaction in the moving heterogeneous system cement–metakaolin–water, especially in its initial steps. This allows a more precise determination of the optimal conditions by using metakaolin as pozzolanic additive in cement mortars and concretes.

Conclusions

Enriched kaolin from the “Senovo” deposit, Bulgaria, is used as initial raw material to produce powdered MK characterized by high PA, high specific surface area and optimal LOI under the experimental conditions applied in this work. The product needs only a short period of grinding to acquire the most appropriate grain size distribution in view of its use as pozzolanic additive in cement mortars and concretes.

The kinetics of pozzolanic reaction metakaolin–lime is investigated under the experimental conditions, which allow eliminating of the liquid phase diffusion as a rate controlling step. The kinetic analysis is carried out by applying models, corresponding to the nature of process and accounting for the effect of granulometry on the kinetics of total reaction. It is established that the rate of pozzolanic reaction is limited simultaneously by the rate of chemical reaction and the rate of diffusion, i.e., the reaction occurs in a transition regime.

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