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

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Abstract The kinetics of the pozzolanic reaction of enriched kaolin from the "Senovo" deposit (Bulgaria) with lime is the object of this article. The kaolin contains kaolinite as a major clay mineral as well as admixtures of quartz and illite. The experimental data of pozzolanic activity at temperatures of 100 and 23 °C are obtained for different reaction times. The reaction degrees of kaolinite and lime at 100 °C are determined from the pozzolanic activity data using a powder X-ray diffraction analysis. 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. It is found by the kinetic analysis that the rate of entire reaction is limited by the rate of chemical reaction on the reaction surface up to degree of reaction near to 0.4. The rate of penetration of the chemical reaction into the kaolinite particles for this area—from the beginning to degree of reaction 0.4, is determined to be equal to 2.10^{-11} m/s.

Keywords Kinetics · Lime–kaolinite reaction · Pozzolanic reaction

Introduction

The lime stabilization of clays finds broad application in various building and construction activities. The pozzolanic reaction products are similar to those obtained during the cement hydration [1–6]. These products are responsible for the strength of stabilized soils, which, in contrast to concrete, varies in low ranges and changes in time following a complex behavior.

The three main clay minerals in soils, such as kaolinite, illite, and montmorillonite, react with lime with different rates [1]. The montmorillonite possess the highest reaction ability, followed by illite, while kaolinite gives the lowest reactivity in this group. Such a behavior of the pozzolanic components of clays determines the possibility to stabilize with lime a variety of soil materials, which are widespread in the nature.

The lime stabilization of soil materials is due to complex and still not well-studied physico-chemical interactions of the clay minerals with lime [1, 7]. The behavior of each of these minerals is important for the detailed knowledge about the flowing processes as well as to improve the results of its practical application. The reaction of illite with lime by the stabilization of illite-rich soil materials [8] is practically complete for about 4 months [9]. The object of the present study is clay, which contain kaolinite as the major clay mineral. The kinetics and mechanism of this process is studied [10, 11] by controlling the strength and phase composition of the products. The analysis performed in these articles leads to the conclusion that the reaction rate is controlled by the diffusion of the lime reagent through the layer of products formed on the clay particle surface.

The purpose of this article is investigation of the kinetics regularities of the pozzolanic reaction in the system lime–kaolin–water. The problems arising during such study are

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concerned with the complex mineral and chemical composition of the kaolin clays [12]. It is to be expected that, together with kaolinite, some of the admixtures, presented in significant quantities, may react with lime, too. Also, there is a great variability in the grain sizes of these clay materials. The influence of all these factors is taken into account in our experiments and analysis of the results. The experimental conditions are chosen in a way to diminish the influence of diffusion on the reaction rate.

Experimental

Materials and methods

Starting materials for this study are enriched kaolin which is the commercial product of the company Kaolin JSCo from the “Senovo” deposit, Bulgaria, calcium oxide, and sucrose with analytical grade purity. The quantitative mineral composition of the kaolin product is determined by the use of DTA/TG and powder XRD methods as well as by chemical analysis. They show the following content of the major components (in mass%): SiO_2 51.20; Al_2O_3 34.13; Fe_2O_3 0.77; TiO_2 0.36; CaO 0.21; MgO 0.25; K_2O 1.05; Na_2O 0.13; LOI 11.70.

Using the powder XRD phase analysis (DRON 3 M diffractometer, Fe-filtered Co Kα radiation), it is found that the main mineral in the initial kaolin is kaolinite. Illite and quartz are present as admixtures. The powder XRD pattern of the sample is given on Fig. 1.

The semi-quantitative XRD approach is combined with normative calculations based on the chemical analysis to determine the content of quartz in kaolin being 14.2 mass%. The illite quantity is calculated on the base of K_2O content to obtain a value of 7.7 mass%. The XRD quantitative determination gives a close value about 7 mass%.

The DTA/TG analysis is performed on apparatus type STA 781 DTA 675 Stanton Redcroft in air at a heating rate of 10 K/min (Fig. 2). As shown in Fig. 2, the thermal decomposition of kaolinite is in the temperature range 450–600 °C accompanied with a crystalline water separation. The mass loss, calculated from the TG curve in this interval, is 10.6 mass%, which corresponds to 77 mass% content of kaolinite in the initial sample.

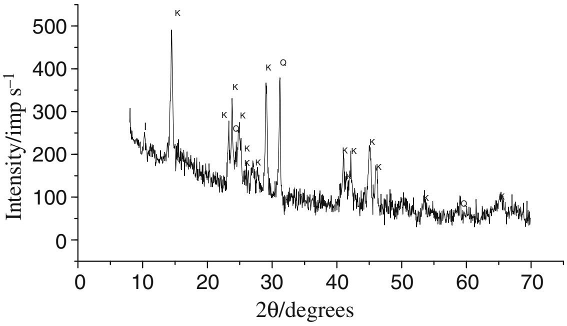

Fig. 1 Powder XRD pattern of kaolin sample from the “Senovo” deposit, Bulgaria. *I* Illite, *K* kaolinite, *Q* quartz

Another endothermal reaction, starting at a temperature of about 550 °C, is related to the dehydration of illite (hydromica) present in the kaolin [1, 13]. The illite decomposes in a high temperature interval characterized with the separation of one molecule of water. This process continues up to about 850 °C. The parallel thermal decomposition of both clay minerals in the temperature range 550–600 °C results in inaccuracy at determining of the kaolinite quantity. This error will not exceed 1–2% due to the low content of illite in the sample and its partial decomposition in the range 550–600 °C with separation of only one water molecule, and for the purpose of this study will not be of significant importance.

The grain size distribution analysis of the fractions greater than 3 μm is performed by dispersion techniques on a Shimadzu apparatus. The experimental data for fractions with grain sizes lower than 3.0 μm was evaluated statistically on a SEM Philips 515. The fraction with greater grain sizes, up to 10–12 μm, consists mainly of quartz grains and aggregates of quartz and kaolinite. The results are summarized in Fig. 3 in the form of a differential granulometric curve. The dashed line represents the upper limit of kaolinite grain sizes.

The kinetics of kaolin–lime reaction is studied by a chemical method, which is based on the Chapelle method for determination of the pozzolanic activity [14, 15]. In order to achieve more repeatable results, the experiments are conducted with 300 mL of water solution of $Ca(OH)_2$ saturated at 20 °C, where the solubility of $Ca(OH)_2$ is 1.65 g/L [16]. A 0.5 g of kaolin is added, a quantity that is almost equal to the content of $Ca(OH)_2$ in the solution. The mixture is then heated up to a temperature of 100 °C and stirred with speed of 150 rpm. The experiments continue from 1 to 24 h.

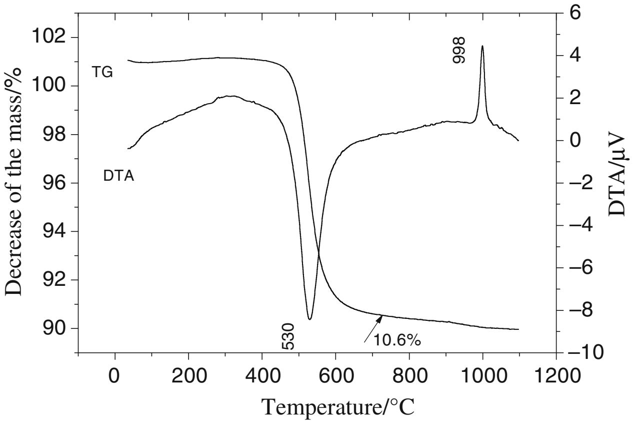

Fig. 2 DTA/TG curves of kaolin from “Senovo” deposit, Bulgaria

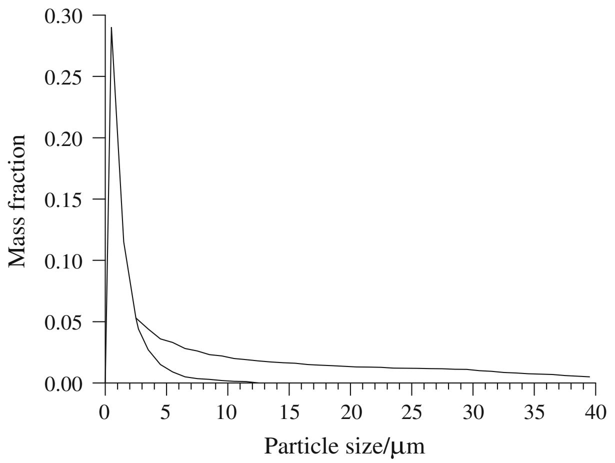

Fig. 3 Differential granulometric curve of enriched kaolin from the "Senovo" deposit

About 50% of the lime content in the solution is transformed into a crystalline phase since the solubility of $Ca(OH)_2$ at 100 °C is only 0.71 g/L. Due to the high rate of dissolution of the $Ca(OH)_2$ at 100 °C, the sediment will regularly restore the quantity of consumed $Ca(OH)_2$ and in this way, the solution will keep constant concentration of $Ca(OH)_2$ during the experiments.

A part of the experiments are performed at a temperature of 23 °C. This is a mean daily temperature for the summer period of this country, close to the temperature of lime stabilization of soil layers in the practice. In these experiments, the starting solution is saturated with lime at 4 °C, where the solubility of $Ca(OH)_2$ is 1.82 g/L.

At the end of experiments, the rest of not reacted lime is extracted from the solid residue with sucrose (in quantity to form 10 mass% solution) followed by quantitatively determination of the $Ca(OH)_2$ content via titration with 0.1 N hydrochloric acid [17]. The following conditions to perform this procedure are found experimentally:

- for the experiments at 100 °C: twice extraction with sucrose at a temperature of 40 °C, stirring with a constant speed at a duration of 2 h in the first stage and 1 h in the second stage (over 95% of the lime is extracted during the first stage and the rest quantity during the second one).
- for the experiments at 23 °C: twice extraction at the reaction temperature, keeping the rest conditions unchanged.

Results and discussion

The data describing the dependence of the pozzolanic activity of kaolin versus time are presented on Fig. 4 expressed as grams reacted $Ca(OH)_2$ per gram kaolin.

A powder X-ray diffraction analysis of a series of samples, subjected to reaction with lime at 100 °C at a different duration, is performed to evaluate the degree of reaction of kaolinite and quartz. The residual contents of both minerals in the samples are determined using the integrated intensities of peaks *001* of kaolinite and *011* of quartz in the powder XRD patterns. Natural hydrothermal quartz with purity of 99.99% and natural kaolinite containing 98.5% kaolinite (the remaining being traces of quartz) are used as internal standards. The powder material in the sample is pelletized to avoid crystals texturing by glue solution and passing the paste through a sieve with openings of 0.10 mm [18].

The XRD analysis showed that quartz practically does not react with lime and must not be accounted for in the kinetic calculations. The degree of reaction of kaolinite, calculated using the XRD analysis data, follows curve 3 as shown in Fig. 4 (as noted above, the admixtures of illite react in a similar way).

The method of Johnson and Mehl [19] is applied in order to determine the rate-controlling step in the entire reaction. This method includes the joined presentation of experimental data and theoretical curves, calculated on the basis of suitable kinetic and diffusion models, in dimensionless coordinates. The dimensionless coordinates in this case are the degree of reaction α and the ratio $t/t_{0.5}$, where t stands for real time and $t_{0.5}$ is the time needed to reach $\alpha = 0.5$.

Gastuche et al. [20] have found for a group of kaolinites with different origin that their kinetics obeys the regularities of homothetically shrinking particles when dissolved in hydrochloric acid. This simplifies the solution of the problem, because the form and the relative size of the particles will not significantly influence the kinetics of the process.

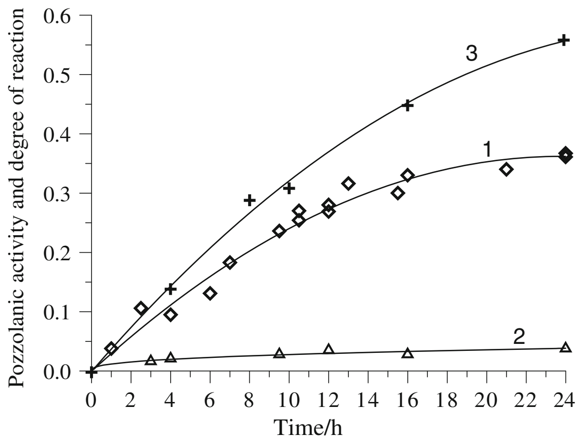

Fig. 4 Experimental data for the reaction of lime with kaolin: pozzolanic activity: 1—100 °C (*diamond*); 2—23 °C (*open triangle*); degree of reaction of kaolinite: 3—100 °C (*plus*)

In the case of poly disperse material, the degree of reaction is a function of the continuation of experiments (t) and the particles size (r_o). For our consideration, kineticr_o is a half of the particle size of all fractions. The kinetic expression, which describes the chemical reaction in the system poly disperse solid material–liquid (or gas) phase, is obtained by integrating of a relation of the type [21]:

$$\alpha(t) = \int_{r_{om}}^{r_{oM}} M(r_o) \cdot \alpha(r_o, t)\mathrm{d}r_o, \tag{1}$$

where r_{om} and r_{oM} are the minimal and maximal radii of the particles, respectively, and the function $M(r_o)$ characterizes the size distribution of particles.

The differential granulometric curve (Fig. 3) is used for determination of the function $M(r_o)$ via summation. The determination of the function $\alpha(r_o, t)$ is performed by successive integration for all fractions and consequent summing up according to Eq. 2 [21]:

$$\alpha(r_o, t) = -\frac{k^3t^3}{2}\int_{kt}^{r_{oM}} \frac{\mathrm{d}r_o}{r_o^3} + 3k^2t^2\int_{kt}^{r_{oM}} \frac{\mathrm{d}r_o}{r_o^2} - 3kt\int_{kt}^{r_{oM}} \frac{\mathrm{d}r_o}{r_o} + 1. \tag{2}$$

The constant k in Eq. 2 represents the rate (in m/s) of penetrating of the chemical reaction in the depth of particles.

A theoretical dependence of the degree of reaction, $\alpha(t)$, for the poly disperse sample is found after substitution of the obtained values for $M(r_o)$ and $\alpha(r_o, t)$ in Eq. 1 and executing of the respective calculations.

The problem concerning the kinetics of diffusion process in the case of poly disperse material has been analyzed by Kapur [22]. The degree of reaction as a function of the time and the particles size are determined by solving Eqs. 1 and 3:

$$\alpha(t) = \int_{r'_{om}}^{r_{oM}} M(r_o).\alpha(r_o, t)\mathrm{d}r_o + \int_{r_{om}}^{r'_{om}} M(r_o)\,\mathrm{d}r_o, \tag{3}$$

where r'_{om} takes consequent values for all fractions in the interval from r_{om} to r_{oM}.

The function $\alpha(r_o, t)$ is determined according the equation of Carter [22, 23]:

$$1 - 3(1-\alpha)^{2/3} + 2(1-\alpha) = k_D t \tag{4}$$

The equation for $\alpha(r_o, t)$ obtained in this manner,

$$\alpha(r_o, t) = 3.98\left(\frac{t}{r_o^2}\right)^{0.47} \tag{5}$$

is used for calculating the theoretical diffusion curve.

Both theoretical curves for reactions, whose rate is limited either from the rate of chemical reaction or from the rate of diffusion, are represented in Fig. 5 in dimensionless coordinates. Based on the proportionality between curves 1 and 3 on Fig. 4, the degrees of reaction of kaolinite are calculated for all experimental results of the pozzolanic activity at 100 °C. They are also presented on Fig. 5 in dimensionless coordinates.

It is evident from Fig. 5 that the kinetics of reaction of kaolinite with lime at 100 °C is limited by the rate of chemical reaction up to $\alpha \cong 0.4$. In the case of higher degrees, the diffusion significantly affects the entire reaction rate.

The value of constant k in Eq. 3 can be determined with inclusion of the substitution [21],

$$\frac{kt}{r_{oM}} = \tau \tag{6}$$

The value of $\tau_{0.35}$ for the degree of reaction $\alpha = 0.35$, determined from the theoretical curve 1 in Fig. 5, is equal to 0.13 ($\tau_{0.5} = 0.225$). This degree of reaction was obtained for 9.5 h; r_{oM} for the kaolinite is accepted to be equal to 6 μm. When introducing these values in Eq. 6, one obtains for the reaction constant a value of 2×10^{-11} m/s.

It follows from the experimental curve for pozzolanic activity at 23 °C (Fig. 4) that the reaction of kaolin with lime proceeds with a very slow rate and α reaches a value of 0.07 after treatment of the material with saturated solution of $Ca(OH)_2$ for 24 h.

Figure 6a and b shows electron microscope photos of the samples treated with lime at both temperatures. In the case of samples treated with lime at 100 °C (Fig. 6a), the primary products of reaction form a layer, in which

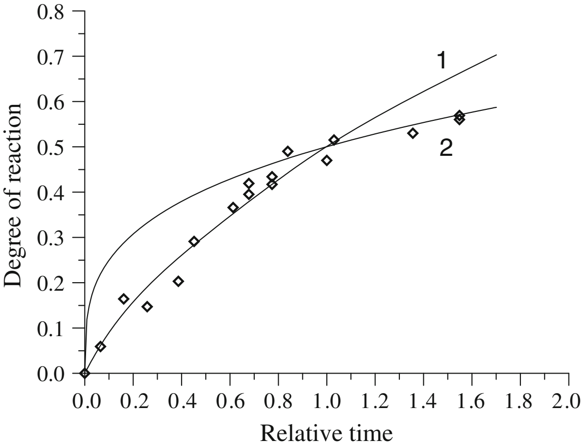

Fig. 5 Experimental data and theoretical curves in dimensionless coordinates: 1—chemical reaction curve; 2—diffusion curve. Relative time = time related to the time needed to reach degree of reaction 50%

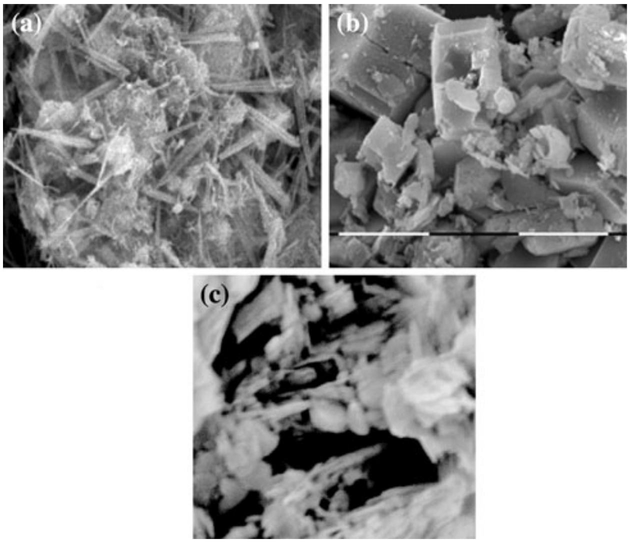

Fig. 6 SEM photos of samples treated with lime: **a** 100 °C, 24 h, ×4000; **b** 23 °C, 5 h, ×3000; **c** 23 °C, 24 h, ×4000

secondary minerals with a needle-like outlook are crystallized. In contrast to them, the samples treated at 23 °C give products that do not form a layer around the particles, but only separated regions on the surface have been take part in the reaction. The start of crystallization in these regions is observed in the form of single needles only for samples treated for 24 h of reaction time (Fig. 6c).

Conclusions

The obtained data for the kinetics of reaction of kaolinite with lime at 100 °C are characterized with a relatively high rate during the first 24 h. The kinetics analysis shows that the mechanism of this process changes gradually as the reaction proceeds in the depth of kaolinite particles: at the beginning, it is limited by the rate of chemical reaction on the reaction surface up to degrees of reaction $\alpha \cong 0.4$, to end after that as a diffusion-controlled process. The rate of chemical reaction at the reaction phase boundary at a lower degree of α is characterized by constant $k = 2 \times 10^{-11}$ m/s. This implies that, at higher temperature, the layer of crystallized products ensures permeability for transportation of the lime reagent from the solution volume to the reaction surface.

At a temperature of 23 °C, the reaction products are localized on some fixed places on the kaolinite particle surface. This probably means that the rate of pozzolanic reaction significantly depends on the density of active centers on the reaction surface.

The knowledge about the reaction kinetic in the system lime–kaolinite–water and of similar interactions of lime with other important natural and artificial pozzolanas has both theoretical and practical significance, because it outlines possibilities for more precise evaluation of the pozzolanic properties of such minerals. On this base, it is possible to forecast the behavior of pozzolanas in cements and concrete as well as during the stabilization of soils.

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