Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 2, 487–490

LIME STABILIZATION OF CLAY FROM THE 'MIRKOVO' DEPOSIT
Part I. Kinetics and mechanism of the processes

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The kinetics of the pozzolanic reactions of illite clay from the 'Mirkovo' deposit with lime is studied using X-ray, DTA/TG, optical and electron microscopy methods. In parallel, the compressive strength properties of the specimens, stored under appropriate conditions for up to 6 months, are measured. Illite reacts almost completely with lime for about 3 to 4 months. The reaction of kaolinite takes place slowly and only about 2/3 of its quantity transform for the 6 months storage period.

The hardened amorphous hydrosilicates and hydroaluminate are formed through the pozzolanic reactions and contribute to the mechanical properties of the stabilized clay specimens. The maximal compressive strength obtained at the experiments reaches about 5–6 MPa. At the end of the storage period, the formation of fibrous or prismatic crystallites is observed on the surface of the particles.

Keywords: *cover systems, kinetics of pozzolanic reactions, lime stabilization of clay, soil stabilization*

Introduction

The stabilization by chemical additives of soil materials with increased content of clay components finds broad application in various construction activities [1, 2]. A similar problem exists also when building up water-impervious insulating layers for sealing of waste dumps [3]. The various types of clays and also some easily accessible and less valuable clay-soil materials can be included in the group of soil materials applied to these purposes. Cement, lime, and fly ash from thermal power plants are usually employed as stabilizing chemical additives [4, 5]. The replacement of cement by lime or by mixtures of lime and fly ash is of particular interest due to the lower price of these stabilizing additives.

The stabilization processes depend on various factors, e.g., on the structure, the mineral and the granulometric composition of the soil material, as well as on the amount and type of the additives. For this reason, the changes in the properties of stabilized soil materials are determined experimentally for each soil type. The knowledge of the processes of chemical interaction of the clay minerals with lime and fly ash is of prime importance for the prediction of the stabilized product properties since these processes are essential for the stabilization.

In the present study, clay of the 'Mirkovo' deposit was used. The interaction of the clay components with lime should be investigated in order to estimate the effect of the processes taking place during this interaction on the physico-mechanical properties of the stabilized product. In this way, further routes to the increase of the rate of these processes could be sought in order to achieve higher intermediate and final strengths of the stabilized material.

Experimental

Materials and methods

A representative sample from the 'Mirkovo' deposit (near to Pirdop, Bulgaria) is studied in order to establish the chemical and mineral composition of the clay. According to the chemical analysis, this material has the following composition (in mass%): SiO_2 – 60.26, Al_2O_3 – 15.05, Fe_2O_3 – 5.24, CaO – 5.02, MgO – 2.77, K_2O – 2.78, Na_2O – 1.75, Li_2O – 6.36.

The mineral composition of the clay is studied by means of X-ray diffraction (Fig. 1) and by optical microscopy. The studies are carried out on a DRON 3M diffractometer and with immersion preparations on a LEITZ polarizing microscope. The mineral composition of the clay material assessed from the data of the X-ray analysis, the optical observations and the calculations of the data from the chemical analysis is (in mass%): quartz – 45, illite – 18, plagioclase (andesine–labradorite) – 14, kaolinite – 5, calcite – 4, potassium feldspar – 12, dolomite – 2. Admixtures of montmorillonite and pyrite, as well as traces of chlorite are also proved.

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1388–6150/$20.00

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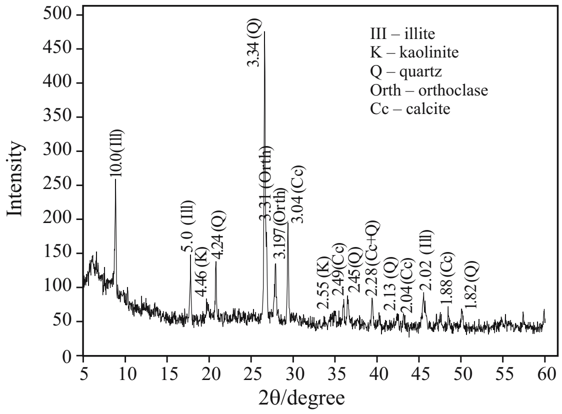

Fig. 1 X-ray diffraction pattern of powdered clay sample ('Mirkovo' deposit)

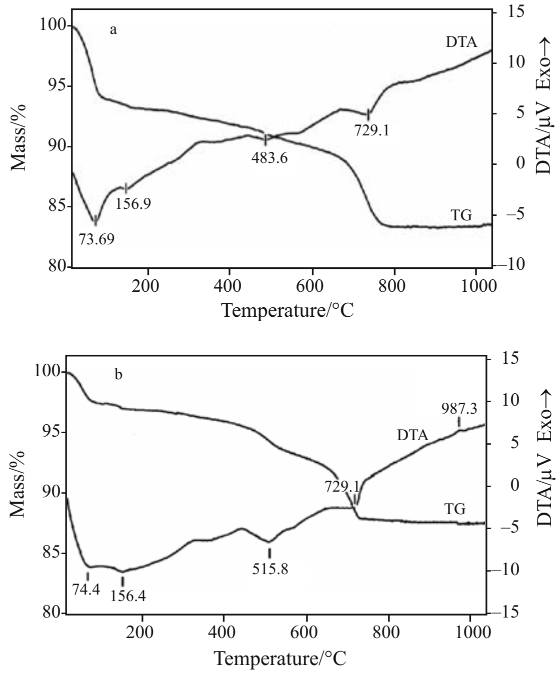

Fig. 2 DTA/TG curves of: a – clay and b – clay-dressed kaolinite mixture samples

The kaolinite content in the clay is determined also by DTA/TG analysis (Fig. 2) on a Stanton-Redcroft 675 equipment in air atmosphere at a heating rate of 10 K min^{-1}. (The observed shifts of the characteristic temperatures in the two DTA curves, Figs 2a and b, are due to differences in the regime conditions.)

The characteristic peaks in Fig. 2a indicate the presence in the clay of illite – 430.1 K (156.9°C), kaolinite – 756.8 K (483.6°C) and alkali-earth carbonates – 1002.3 K (729.1°C) [6, 7]. Water is separated at a lower characteristic temperature of 346.9 K (73.7°C). The peak at 1260.5 K (987.3°C) in Fig. 2b also belongs to kaolinite.

Due to the low kaolinite content and the complex mineral composition of the clay, an indirect method is used for the determination of the kaolinite content, consisting in the addition of 8–10 mass% enriched kaolin of the 'Senovo' deposit as an internal standard. The standard additive contains 79 mass% kaolinite, the rest being β-quartz and feldspar. The total amount of kaolinite (available and added) in the sample is determined from the area of its dehydration characteristic peak at 789 K (515.8°C) in Fig. 2b, due to the stoichiometric reaction [8, 9]:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \rightarrow Al_2O_3+2SiO_2+2H_2O$$

The difference between the total and added kaolinite gives its content in the clay. Thus, the kaolinite content in the starting clay is determined to be 5.5 mass%.

The quantitative determination of illite by means of DTA/TG analysis proved impossible due to the fact that, according to literature data [6, 7] and our experimental results, illite decomposes within a broad temperature range with separation of water, and this process is not complete even at 1100 K. Because of the overlapping of the effects of this process and the decomposition of carbonates, their amount cannot be determined. For the accurate determination of carbonates, the direct trapping and analysis of evolved CO_2 is required.

The content of organic substances in the clay, calculated as organic carbon, is analytically determined [8] and amounts to 0.9 mass%.

The granulometric composition of the clay is determined by sieve analysis (Bulgarian State Standard 2762/75) and the fractions with size of –0.100 mm were determined by dispersion analysis on a Shimadzu apparatus. The experimental results for the basic fractions (in mass%) are as follows: gravel (+2 mm)–5, sand (–2+0.1 mm)–36, silt (–0.1 +0.005 mm)–33, clay (–0.005 mm)–26.

On the basis of the data from the chemical, mineral, and granulometric analysis, the clay from the 'Mirkovo' deposit can be classified as sandy-silty, with low humus content; the basic clay component is illite.

Interaction with lime of the clay components from the 'Mirkovo' deposit

The kinetics of clay interaction with lime has been carried out so far by experimental determination of the compressive strength. What is more, the data reflecting the illite behaviour are quite restricted [10–12]. One can conclude from these investigations that the time dependence of the compressive strength has a specific nature due to the effect of various factors, such as the mineral composition of soil materials, the type and amount of the lime additive, the experimental conditions, etc.

In the present work, the kinetics of interaction of the clay components with lime is directly studied. Investigations of the increase of the unconfined dry compressive strength are carried out in parallel. For conducting the tests, sample specimens are prepared, consisting of a homogeneous mixture of clay from the 'Mirkovo' deposit and slaked lime inserting 8 mass% $Ca(OH)_2$. This amount of the additive is chosen from practical considerations, since the optimal lime additive determined by a pH test [13] is 5 mass% $Ca(OH)_2$. At such a mass content, however, the rate of the pozzolanic reactions determining the strength of the stabilized material remains quite low. On the other hand, at a higher $Ca(OH)_2$ content (above 10 mass%) problems can arise, related to the cost effectiveness of the use of stabilized soil materials. Furthermore, according to some authors [5], a decrease in the strength characteristics is observed by the addition of 15 mass% lime to the mixture.

The sample specimens are prepared by compaction of the material at the optimum moisture content according to the requirements of Bulgarian State Standard 3214/75. The sample specimens are kept in a closed thermostatic vessel in order to restrict the access of CO_2, at a temperature of 298±1 K, the atmosphere in the vessel being saturated with water vapours.

The reaction degree of illite is estimated by means of X-ray data. Figure 3 shows a comparison of the basic lines of illite (d=1.00 nm) and quartz (d=0.334 nm) for the clay mixture containing 8 mass% $Ca(OH)_2$. In order to restrict the predominant orientation of the particles, the sample is granulated with shellac through a 0.10 mm sieve according to the method of Petrov and Kirov [14].

The decreasing height of the basic illite peak in Fig. 3 suggests that the reaction of illite with lime is practically complete for about 3 to 4 months. Kinetic data on the kaolinite reaction with lime are presented in Fig. 4.

Figure 4 shows that the kaolinite reaction with lime has a lower rate than that of the respective illite reaction. During a 6-month storage of the test specimens, only about 2/3 of the clay mineral take part in the reaction.

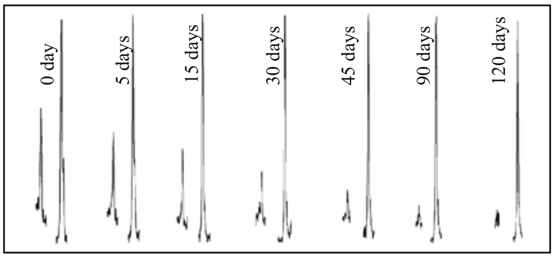

Fig. 3 Comparison of the basic lines for illite (d=1.0 nm) and quartz (d=0.334 nm) for mixtures of clay and 8 mass% lime stored at 298 K for various time periods

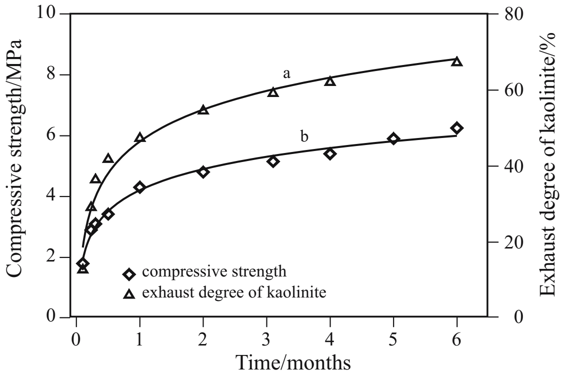

Fig. 4 Kinetic data on the rate of a – interaction of kaolinite with lime and b – on the rate of increase of the unconfined compressive strength

The unconfined compression strength was tested on a FPZ 100/1 equipment with dry specimens immediately after their removal from the thermostat. All experimental data on the compressive strength are obtained as mean arithmetical values from three tests. The averaged results are given in Fig. 4.

The kinetic curves of the kaolinite reaction with lime (the data concerning illite have a semiquantitative nature) and of the increase of the compressive strength have the same trend, characterized by the existence of two periods:

- an initial period of about two weeks, characterized by a more intensive occurrence of the respective processes;
- a subsequent period of a slower increase of the strength as well as a lower rate of the reaction between kaolinite and lime.

The kinetic data on the interaction of the clay components with lime can be explained by the mechanism of the pozzolanic reactions taking place. The reactions between the clay minerals and lime lead to the formation of gelated calcium hydrosilicates of the C–S–H type and of calcium hydroaluminate of the CAH type. The calcium hydrosilicates contribute substantially to the strength of the stabilized soil material and are of varying composition [1, 15–19]. The CaO/SiO_2 molar ratio in the hydrosilicate phase varies within quite broad limits from 0.8 to 2.2 depending on the amount of free lime in the system. During the more intensive interaction of the clay minerals with lime and water, which is characteristic of the initial stage of the process when a sufficient amount of free lime is still present in the system, the richer in lime hydrosilicate is formed [4]. Figure 4 shows that during this period the strength reaches about 50% of its final values and forms the initial strength.

The next stage is characterized by a slower increase in strength, accompanied by an in-depth penetration of the pozzolanic reaction into the clay

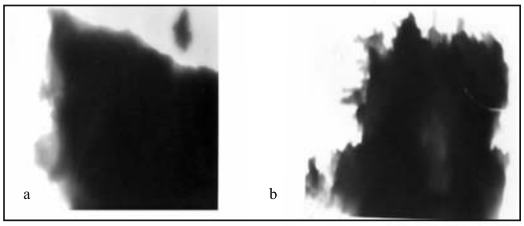

Fig. 5 TEM micrographs of a – amorphous material after storage for 3 months and b – slightly crystallized material after storage for 6 months

mineral grains. Due to the fact that the non-decomposed grain kernels are embedded into the products of the pozzolanic reactions, diffusion makes possible the transfer of the reagents (free lime and water). This mechanism is in agreement with the parabolic trend of the kinetic curves.

By a chemical analysis it is established in [1] that under similar conditions the free lime in the system is completely exhausted for about 6 to 12 months. By the end of this period, the pH values of the system decrease to ≤ 11 and the CaO/SiO_2 molar ratio tends to the lower values of ≈ 0.8 [1, 16].

The pozzolanic reactions take place for long time periods, also after the depletion of the free lime [19]. According to [16], at this stage the reaction is possible at the expense of CaO from the initially formed and richer in lime hydrosilicate phase, by a diffusion transfer through the layer of reaction products to the non-decomposed kernels of the clay particles. Phase changes of calcium hydrosilicates take place simultaneously and these two processes lead to a slow increase in strength with time.

The formation of new phases and crystalline products is proved by TEM analysis on a PHILIPS-400 equipment under the following conditions: U–80 kV and magnifications of 7000/33000×.

Clay mineral particles covered by a layer of pozzolanic reaction products are shown in Fig. 5. The analysis of the products of the interaction between the clay components and lime after storage of the sample specimens for 1 to 3 months suggests that they are fully amorphous (Fig. 5a). After storage for 5 to 6 months, the formation of fibrous or prismatic crystallites is observed to start on the surface of the particles (Fig. 5b). This is assumed to be the initial stage of the changes in the phase composition of the gelated calcium hydrosilicates [1].

Conclusions

The data on the interaction of the clay from the 'Mirkovo' deposit with lime suggest that, under the experimental conditions chosen, the increase in strength during the first 6 months is due entirely to the initially formed and hardened gelated products of pozzolanic reactions involving mainly the clay minerals. A stabilized soil material is obtained with dry unconfined compressive strength of the order of 5 to 6 MPa. The processes causing changes in the phase composition of the calcium hydrosilicates take place at longer storage times. These processes are characterized by a low rate and can lead to higher compressive strength values after prolonged storage.

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Received: December 13, 2006
Accepted: June 5, 2007

DOI: 10.1007/s10973-006-8304-9