Effect of Heat Treatment on Phase Compositions of Clay Aluminosilicates

Mikhail Lebedev, Igor Zhernovsky, and Valeria Strokova

Abstract One of the methods of activation and modification to improve quality characteristics of raw materials is a thermal treatment that was used for property improvement of clay materials in this work. For this purpose the treatment thermal interval of 500–600 °C, allowing getting the material with stable properties when thermal treatment and high adsorptive activity was used.

The goal of this work is to study the mechanism of the processes occurring in these polymineral systems and contributing to positive changes in properties. According to X-ray and IR-spectroscopy analyses data for samples exposed to treatment at the temperature of 500 °C the transformation of the crystal structure of layered aluminosilicates, mainly kaolinite as 2D-nanoparticles into the frame aluminosilicates of zeolite group – 3D-nano-objects, in particularly, faujasite with size of crystallites about 80 nm (according to the X-ray analysis) is performed.

The change in the particles shape is observed: bonded clay minerals transfer to isometric formations, typical to minerals of zeolite group.

Keywords Clay aluminosilicates • Heat treatment • Zeolite • X-ray and IR-spectroscopy analysis • Microstructural analysis

1 Introduction

At the present stage of development of construction material science for improvement of composites characteristics, more popular becomes the application of different methods of activation and modification for quality improvement of raw materials. One of such methods is a thermal modification that was used for property improvement of clay materials in the frame of this work. For this purpose the

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temperature interval for treatment was determined as 500–600 °C, allowing getting the material with water-stable characteristics and high adsorptive activity [1, 2].

The research presented in this article focused on extension of assortment of raw materials for production of the filler of asphalt binder and asphalt concrete due to utilization of widely distributed raw materials such as sedimentary aluminosilicate rocks.

The objective of this work is to understand a mechanism of behavior in the polymineral systems that stimulating a favored changing in properties of the systems.

2 Experimental

2.1 Materials and Methods

In this research polymineral sedimentary rocks from South Ural were used. These materials include coal-bearing course of Korkino deposit, which are characterized by significant chemical and species composition associated with conditions and location of formation. For the purpose of generalization, the study was carried out with using one species of the rocks.

Qualitative evaluation of the phase composition for aluminosilicate raw was carried out with XRD analysis on the diffractometer DRON-4 (Russia) with using of CuAβ radiation. The full-width at half-maximum (FWHM) of these patterns was 0.05°. Interpretation of the diagrams and identification of the composing minerals were made with using of ICCD data base and Crystallographica Search-Match (Oxford Cryosystems) software. In this work also was used FTIR-spectroscopy (VERTEX 70, Bruker Optics, Germany). Microstructural analysis of the samples was carried out by SEM (Supra 50 VP, Germany) with analytical system INCA Energy + Oxford. SEM analysis of the samples was run without sputtering in the conditions of alternating pressure.

2.2 Samples Preparation

The main practical relevance of the research is in the study of thermal treatment influence on phase composition of clay materials used in this work. The thermal treatment presented by gradual heating up of initial material (bulk material) till required temperature, followed by thermal exposure for 2 h with gradual cooling down after that.

In order to estimate changing in composition and structure of the studied polymineral aluminosilicate rocks in dynamic, mineral composition, FTIR-spectroscopy and microstructure of the materials were investigated in an initial condition (previously, the specimens were milled in a ball mill for short time till the Blain specific surface of 430 m^2/kg) and after thermal treatment at 400, 500 and 600 °C (after thermal treatment the specimens were milled in a ball mill for short time till Blain specific surface of 600,610 m^2/kg).

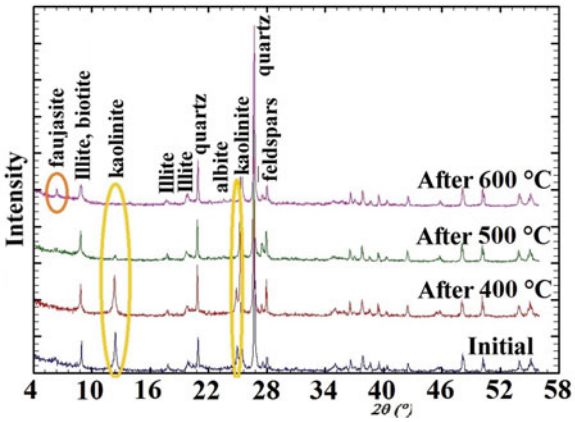

Fig. 1 X-ray diagram of aluminosilicates before and after treatment at 400 °C, 500 °C, 600 °C

3 Results and Discussions

3.1 XRD Analysis

According to XRD data, in the mineral composition of the initial specimens (Fig. 1), there are crystal phases of quartz, kaolinite clay, illite, biotite and feldspars. It should be noted, that some portion of rocks substance is X-ray amorphous including carbon-bearing impurities.

In compliance with obtained data, a thermal treatment of the initial materials induces changing in the mineral composition and, as a consequence, allowing getting the material with water-stable characteristics and high adsorptive activity [1, 2].

According to XRD data, after the thermal treatment at 500–600 °C, a transformation of crystal structure of layered silicates occurs. Mostly, the crystals of kaolitite clay with 2D-nanoparticles, according to traditional conception, get forming the minerals of zeolite type – 3D nanoobjects, mainly faujasite mineral (Fig. 1). That is confirmed by the factor, that with increasing of the temperature during thermal treatment, a significant reducing of reflections of kaolinite happens after 500 °C till full disappearing after 600 °C that can be seen on the X-ray diagrams for aluminosilicate (Fig. 1). A disappearing of kaolitite leads to formation of new, mainly, framework silicates. Mostly, they presented by high dispersed phases, which, because of their small size are invisible for X-ray diffraction. Thanks to certain conditions, it became possible for such X-ray amorphous minerals to get bigger, that induced the appearing of faujasite reflections. Based on XRD data, the size of crystallites of that zeolite was calculated that is about 80 nm.

It is necessary to mention, according to studies of the other researchers [3, 4], in the temperature interval of 500–600 °C aluminosilicate raw with similar composition may be synthesized to identical framework new formations.

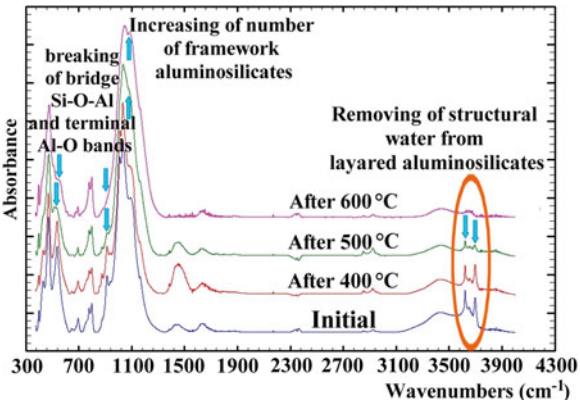

Fig. 2 FTIR-spectrum of the aluminosilicates with different Al_2O_3/SiO_2 ratio before and after treatment at 400 °C, 500 °C, 600 °C

3.2 FTIR-Spectroscopy Analysis

The mineral composition of the studied specimens is confirmed by IR-spectrums (Fig. 2). For the analyzed probe in initial condition the presence of aluminosilicate structural arrangements Q^3 typically prevails [5].

Thermal treatment of the material affects the structure with changing on molecular level. This is proved by IR-spectroscopy data of aluminosilicate materials after different thermal treatment (Fig. 2).

The analysis of the obtained IR-spectrum showed that increasing in temperature leads to changing of absorption band for aluminosilicate groups. Based on XRD data, after thermal treatment at 500 °C a transformation of crystal structure of layered silicates occurs followed by formation of zeolite type of minerals. To confirm this statement, it can be considered the shift of the absorption band of layered anions to the region with bigger wavenumbers from 1,035 to 1,053–1,067 cm^{-1}, which is evidence of increasing in polymerization degree of silicate system [6, 7] (Fig. 2). This is followed by a significant growth of absorption band intensity of framework structures Q^4 synchronous spreading of all "Si-O" profile in the region of 1,100–1,300 cm^{-1}.

Gradual decreasing of an intensity of the bands 915, 947 and 537 cm^{-1} can be explained by breaking of bridge-links Si–O–Al [8] as well as unbridge-links Al–O in the alumo-oxide octahedrons of kaolinite layered structures followed by dehydration, that can be confirmed by reducing of absorption bands intensity on the region of 3,600–3,700 cm^{-1} (Fig. 2). Herein, the transformation of Al from octahedron (AlO_6) coordination to tetrahedron (AlO_4) occurs. Appearing of the band at 556–560 cm^{-1} after thermal treatment at 600 °C can be explained by formation of double quaternate rings in the structure of zeolites with transformation of Al into tetrahedron orientation [9].

3.3 SEM Analysis of Microstructure

The effectiveness of the thermal modification on the studied aluminosilicate materials is justified by microstructural analysis.

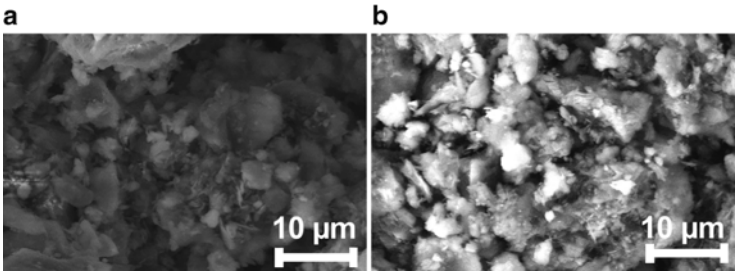

Fig. 3 Microstructure of the filler: (**a**) without thermal treatment; (**b**) with thermal treatment

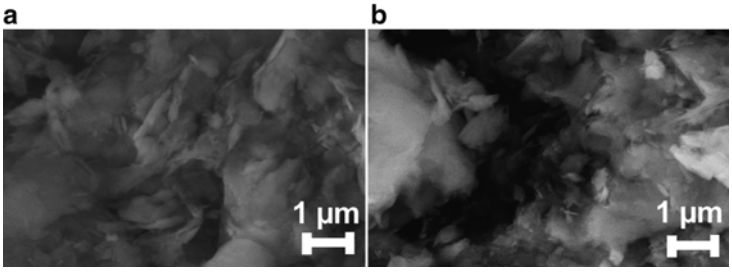

Fig. 4 High dispersed substance in the structure of aluminosilicate: (**a**) without thermal treatment; (**b**) with thermal treatment

To estimate the affect of thermal treatment on the raw a comparative analysis of microstructure of the filler at different conditions: after mechanical treatment and thermal modification of the initial materials followed by dispersion.

Mineral composition of the initial material, mainly, prevailing of clay minerals provides a high dispersity of obtaining filler (with Blain specific surface 430 m^2/kg) (Fig. 3). Analyzing the SEM pictures, it can be concluded of polyfractional particle distribution (Fig. 3a). As we can see, there are coarse particles with the size of 20–25 μm, but mostly the particles are presented with average size no more than 5 μm.

According to the obtained data, thermal treatment leads to increasing in specific surface and to growth of particle, related to synthesizing of new formations on the system and slight particle aggregation. That happens due to reducing of extra energy in the system induced by dehydration of layered aluminosilicates. The particle growth is proved by SEM data (Fig. 3b). The main portion of the system is presented by the particles with the size of 20–30 μm that have a high strength and because of it they can be appeared for building of a framework in bitumen-mineral compositions. The same morphology has a most part of the particles of modified mineral powder (Fig. 3b). Probably, a highly-developed surface can provide a high summary specific surface of the filler (with Blain specific surface of 610 m^2/kg).

When considering a highly-dispersed portion of the filler, it is necessary to note, that in the specimen without thermal treatment, particles with size of 200–300 nm are presented by clay phases on the form of thin flake-like pallets (Fig. 4a). Most likely, that X-ray amorphous substance can be a product of uncompleted mineral

formation stage. Because of the structure, it is highly reactive materials that may react to organic binder and water as well.

Thermal treatment gives a quality effect to fine phases. It was found, that after modification instead of thin pallets of the clay phases in the specimens appear isometric new formations (Fig. 4b), which may be attributed to zeolite type of minerals, the presence of with was confirmed with using XRD analysis. The size of those formations is slightly bigger than that of initial clay substance, where the size of a separate particle is about 1 μm (Fig. 4b). In accordance with composition and structure such type of material would be active components in the bitumen-mineral compositions.

4 Conclusions

Mineral powder based on aluminosilicate raw of clay composition is a highly-dispersed component in the bitumen-mineral compositions that provides its chemical activity to organic high-molecular compounds and to water. After water impaction, the characteristics of the composites get significantly worsen. But, at the same time, thermal activation of the compositions allows getting the material with water stable properties and high absorptive activity, that improves an adhesion between bitumen and particle surface and as consequence provides an advancing of physical and mechanical characteristics of asphalt binders and asphalt concretes. That happens due to changing in phase composition of mineral material, where a transformation of crystal structure of layered aluminosilicate takes place. Kaolinite transforms to framework aluminosilicates of zeolite type.

Therefore, understanding the mechanism of modification and activation of the materials, including non-conditioned materials, it is possible to improve the characteristics of the components of construction materials and composites their base.

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