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Modified Glauconites of Republic Kazakhstan and Their Sorption Properties*

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Abstract

Glauconite and glauconite sand were used as starting materials. To prepare adsorbents on the ground of glauconite, mixtures of glauconite sand and sodium dihydrophosphate NaH_2PO_4 at various weight ratios (1 : 1, 2 : 1, 3 : 1, 4 : 1) were subjected to the mechanical activation (MA) in a planetary mill. MA products were studied by methods of X-ray phase and thermal analysis. Degrees of sorption for ions of manganese, cuprum, nickel and zinc were determined from appropriate solutions of sulphates within the concentration range of 60–1000 mg/L.

Key words: glauconite, glauconite sand, sodium dihydrogen phosphate, mechanical activation, sorbents, fertilizers, microelements

INTRODUCTION

It is known that clay minerals include various groups of aluminosilicates whose main types of which pass from one into another. Glauconite (G) represents a potassium-containing aqueous aluminosilicate with an averaged formula $K_{<1}(Fe^{3+},Fe^{2+},Al,Mg)_{2-3}[Si_3(Si,Al)O_{10}][OH]_2 \cdot nH_2O$, a mineral belonging to the group of hydromicas, subclass of layered silicates, having a variable complicated composition. It belongs to the most widespread and diverse class of minerals consisting of one-type aluminosilicate layers (2 : 1) [1], separated by interlaminar interlayers of not one but various sorts, *viz.*, of K^+ cations ,water molecules and exchangeable cations [2–5].

Highly sorption properties of glauconite [5–10], relatively to ions Zn, Mn, Ni, Cu, Co(II), in which there is a lack of most soils of Kazakhstan, were used as direct potassium fertilizers and micronutrients [6, 7], with the purpose of the application of glauconites.

The purpose of this work consisted in studying the sorption properties of modified glauconites derived from common glauconite sands with the use of thermal and mechanochemical methods (in the presence of additives).

It should be noted that the influence of mechanical activation (MA) upon the structure and physicochemical properties of glauconite hitherto is poorly studied.

EXPERIMENTAL

The museum sample of glauconite (the Institute of Geology and Mineralogy of the SB RAS, Novosibirsk), Karatau glauconite concentrate and glauconite sand, that is the waste of the Sokolov-Sarybays ore deposit, was selected as investigation objects. The influence of the mechanical activation (MA) on the structure and physical-chemical properties of

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glauconite is virtually unexplored. For MA we used a Pulverisette 6 programmable planetary-type mono-grinder with stainless steel fittings (planet gear carrier rotation frequency ranging within 100–600 min^{-1}). The internal dimensions of the drum were as it follows: height 7 cm, diameter 10 cm, capacity 500 cm^3; the radius of the balls 0.5 cm, the number of balls 109 pcs. For the MA treatment of glauconites and glauconite sand mixtures with sodium

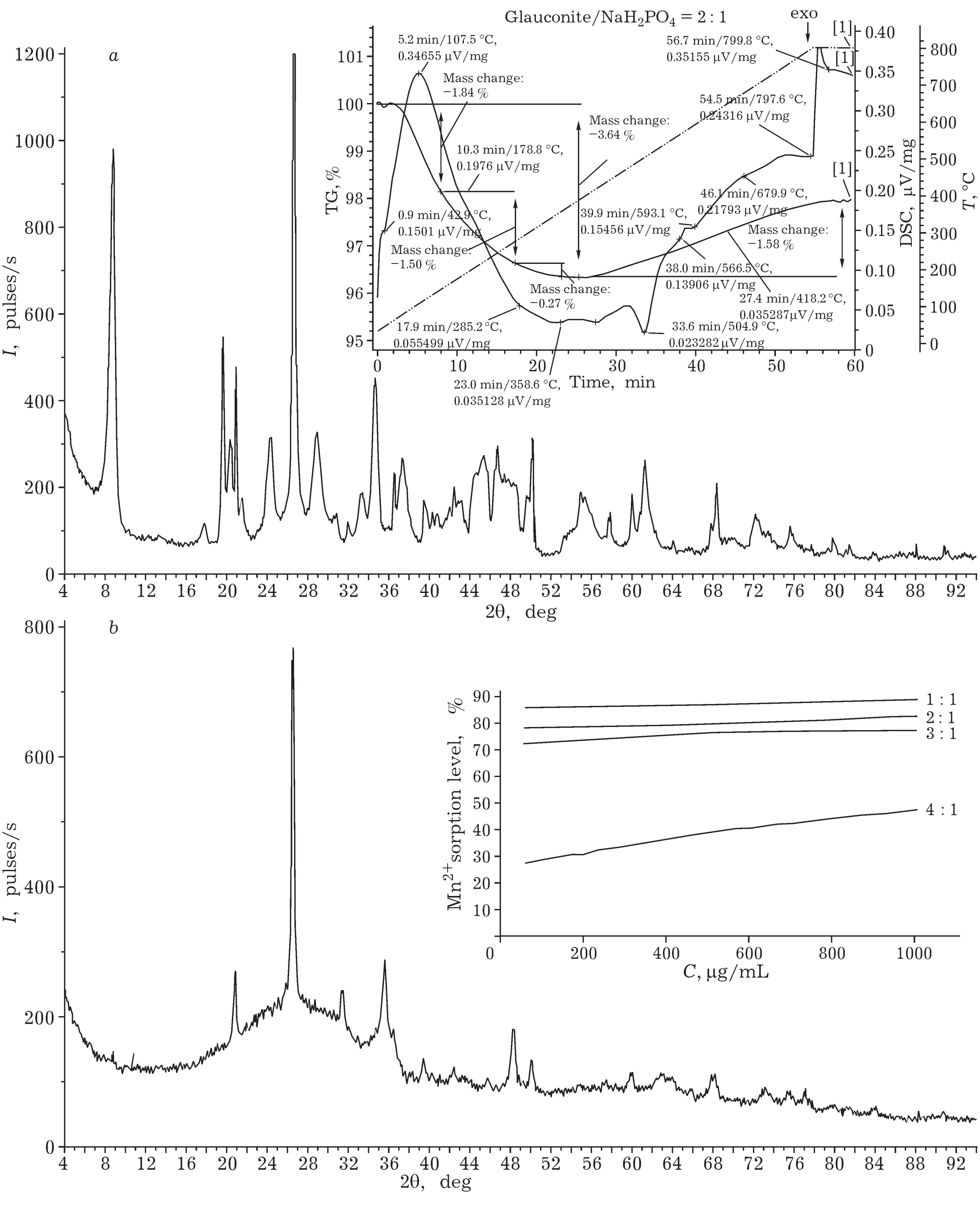

Fig. 1. XRD profiles (CuK_α radiation) for the original (*a*) and mechanically activated (*b*) museum sample of glauconite. Insets: *a* − thermal analysis data for MA mixture (2 : 1); *b* − the level of sorption by mechanically activated mixtures for Mn^{2+} ions depending on the concentration of the initial solution.

dihydrogen phosphate (NaH_2PO_4) in various mass ratio values (1 : 1, 2 : 1, 3 : 1, 4 : 1) we used weighed sample portions with the mass equal to 24 g.

We have chosen a unified mode of the mechanical treatment, for example, for mixture 1 : 1.

– "Homogenization" at 140 min^{-1} for 7 min, 1 min pause, reverse, 3 repetitions, total time 28 min; uncovering, examination, restacking (in order to exclude MA sintering the material at the bottom of the drum).

– Grinding at 210, 280, 350 min^{-1} for 7 min, 1 min pause, reverse, one repeat; total time 42 min, examination, restacking.

– Grinding + MA under the mode of "grinding" at 420 min^{-1} (examination, restacking), that at 490 min^{-1} (restacking), that at 560 min^{-1} (completion); the final MA duration was equal to 112 min.

Characteristics of samples obtained were studied by means of standard methods of XRF phase analysis, thermal analysis (TG, DSC, DTA, in nitrogen atmosphere), and X-ray fluorescence analysis, as well as thermal annealing.

RESULTS AND DISCUSSION

Figure 1 demonstrates an effect of the MA treatment of the museum glauconite sample on its structural characteristics. XRF data for glauconite concentrate and sand differ only in higher quartz content in the sand (Figs. 2, 3). Assuming that the mass loss of the sample is inversely proportional to the content of quartz therein, glauconite sand contains nearly 10 times more quartz than the concentrate (compare mass losses 14.93 % in Fig. 2 and 1.40 %, in Fig. 3.

According to the results of the derivatographic studies performed for all the MA samples (see Fig. 1, *a*, inset), an increase in TG curve is observed after a smooth decrease associated with the loss of the adsorption, crystallization and constitutional water. This indicates that the sample reacts with nitrogen. The increase in the mass of the sample is determined by the initial mass between the NaH_2PO_4 and glauconite sand in the mixture. The maximum nitrogen adsorption inherent in the MA treated sample of the mixture with the ratio equal to 1 : 1 (with the highest content of NaH_2PO_4): the maximum mass loss amounts to

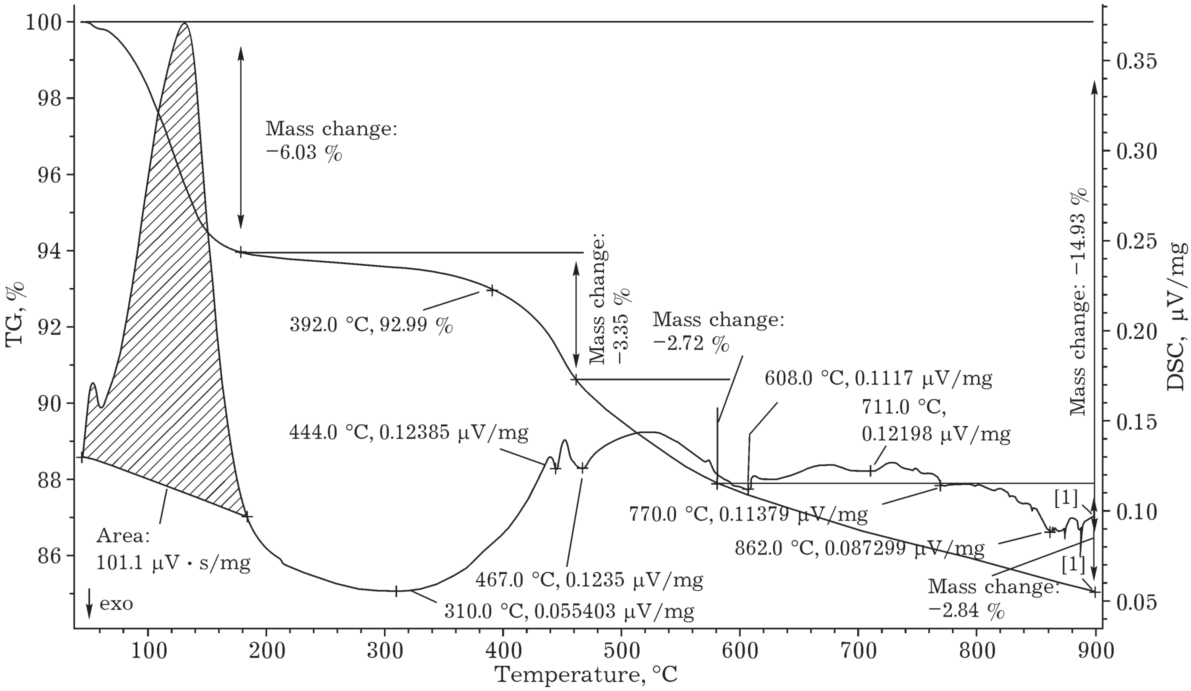

Fig. 2. Thermogravimetry (TG) and differential scanning calorimetry (DSC) data for the original glauconite concentrate.

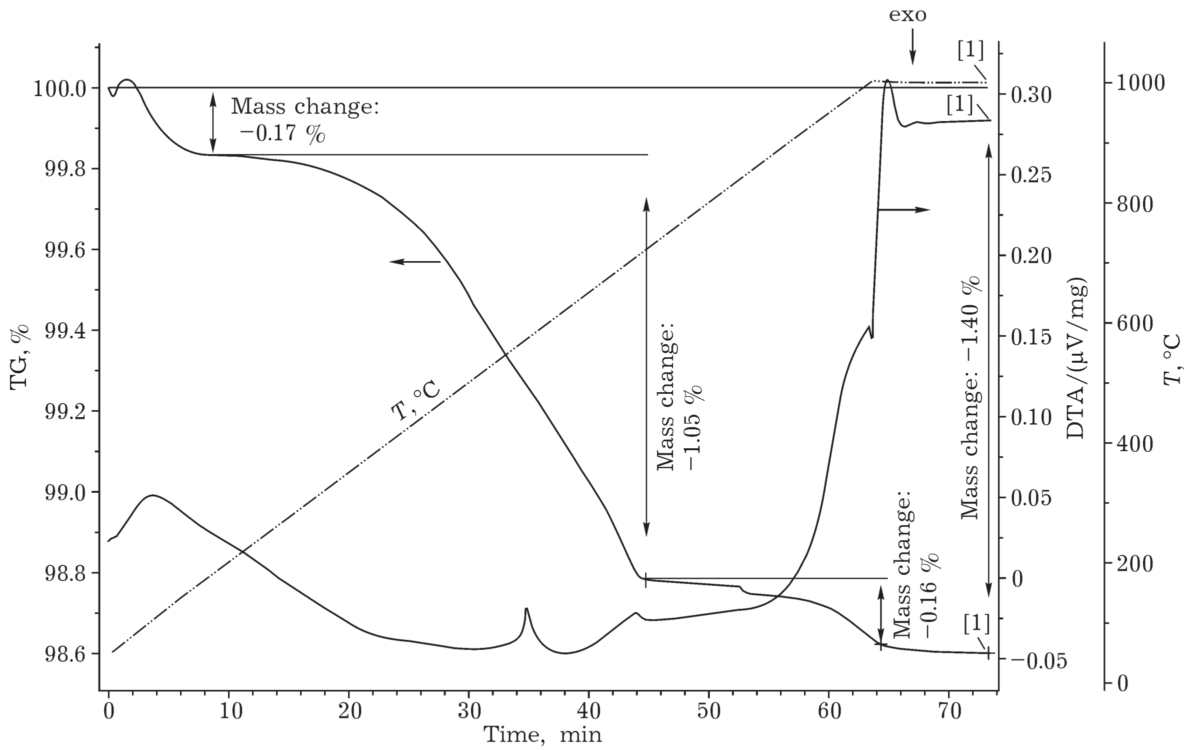

Fig. 3. Thermogravimetry (TG) and differential thermal analysis (DTA) data for the original glauconite concentrate.

3.59 %, the further increase corresponds to 2.78 %. For the samples of glauconite concentrate (see Fig. 2) and sand (see Fig. 3) with no acid salt added such a phenomenon was not observed. Thus, the addition of NaH_2PO_4 significantly affects the sorption properties of the samples.

Data presented in Fig. 2 demonstrate that the thermal effects on DSC curve are observed at about 450 °C (endo) and 900 °C (exo), so, in we chose it is these temperatures were chosen to study the thermal modification of glauconite. DTA data for glauconite sand turned out to be comparable with the results of DSC for the concentrate (see Figs. 2 and 3).

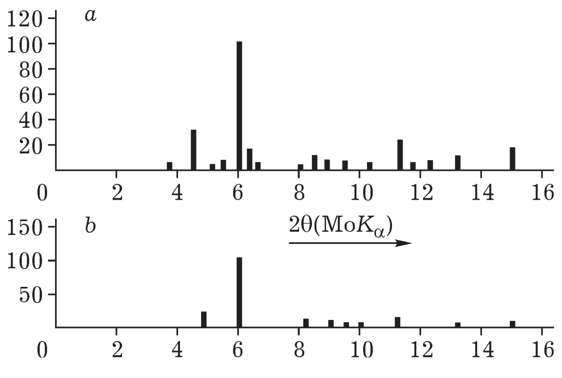

Fig. 4. Data XRF phase analysis data for the samples of glauconite sand: *a* – original sample; *b* – mechanically activated mixture 1 : 1.

According to XRF phase analysis of the both original and thermally treated glauconite concentrate, increasing the temperature results in the appearance and increase of reflexes of hematite and magnetite, while the intensity of lines of quarts decreases. At 450 °C reflexes of glauconite weaken, and at 900 °C (G-900) they disappear completely.

Figure 4 demonstrates a bar chart for the XRF profiles of the original glauconite sand and of the MA treated sample, *viz.*, its mixture with NaH_2PO_4 at a ratio of 1 : 1. It can be seen that after MA many reflections disappear, and the material is partially amorphized (see Fig. 1).

The content of nickel, zinc, manganese and copper in the initial and equilibrium solutions was determined by means of a PerkinElmer Optima 5100 DV optical emission spectrometer with the inductively coupled plasma at the wavelengths of 325, 228, 224 nm. As a reference sample, we used the State Standard sample containing 10 mg/L of nickel, zinc, manganese, copper ions. Figure 5 demonstrates the results of the studies on the sorption properties of the original and modified samples on

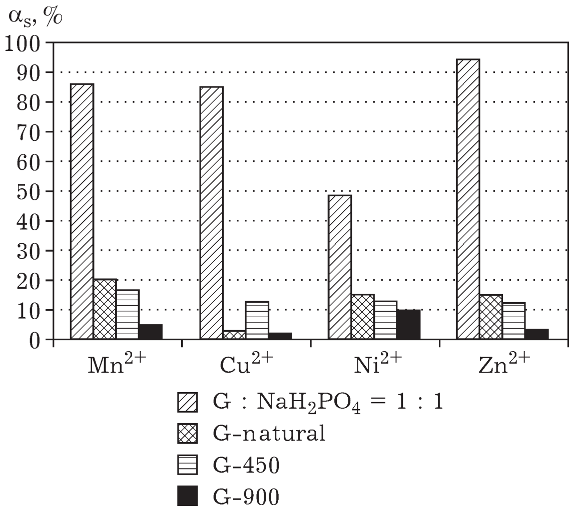

Fig. 5. Changing the level of sorption (α_s) by glauconite sand for manganese, copper, nickel and zinc ions depending of modified glauconite forms obtained.

the ground of glauconite sand (G-natural) performed for aqueous solutions of the corresponding ions at the concentration of 60 mg/L.

It can be seen that the level of sorption α_s with respect to ions in the case of the mechanically activated mixture (1 : 1) exceeds in several times that of glauconite sand decreasing in the order: Zn^{2+} (α_s = 94.9 %) > Mn^{2+} (86.2 %) > Cu^{2+} (85.6 %) > Ni^{2+} (48.9 %). After annealing the glauconite sand, the sorption capacity thereof with respect to these ions decreases, except for copper ions. So, with respect to zinc ions decreases in the order: 15.0 % (G-sand) > 12.0 % (G-450) > 3.4 % (G-900); with respect to manganese ions: 20.4 % (G-sand) > 16.3 % (G-450) > 4.5 % (G-900). With respect to copper one can observe the following trend: 3.0 % (G-sand) < 12.5 % (G-450) > 2.1 % (G-900). It has been found that annealing almost does not affect the process of the sorption of nickel ions by the sample: 15.0 % (G-sand) > 12.6 % (G-450) > 9.6 % (G-900).

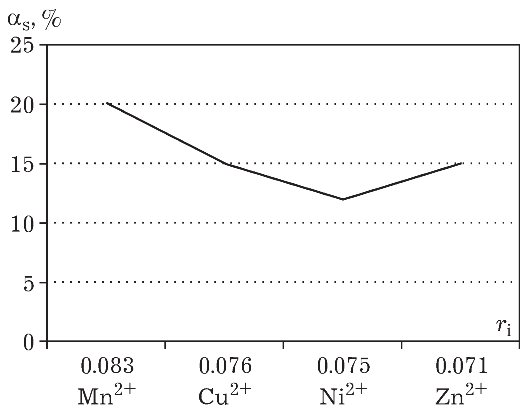

Fig. 6. Sorption capacity of thermally modified at 450 °C mechanically activated mixture 1 : 1 depending on the ionic radius (r_i) of the elements.

The increase of the sorption capacity of the mechanically activated mixture at a ratio of 1 : 1, could be connected with the mechanochemical transformation of the calcium glauconite form into the sodium form thereof by the addition of the acidic salt of NaH_2PO_4.

Figure 6 demonstrates the effect of annealing the MA treated 1 : 1 mixture at 450 °C on its ability of sorption from initial solutions. We attempted to relate α_s with radiuses of metal ions (r_i). It has been established that the sorption degree α decreases in the following row: Mn^{2+} (α_s = 20 %) > Zn^{2+} (15 %) = Ni^{2+} (15 %) > Cu^{2+} (12 %).

By the example of initial solutions with different concentrations of manganese ions we studied the sorption capacity values for the obtained MA treated mixtures of glauconite sand and acid salt NaH_2PO_4 (see Fig. 1, *b*, inset). It can be seen that the level of sorption exhibits an increase with increasing the content of acid salt additive and the concentration of manganese ions in the initial solutions, *i.e.* the sorption level is weakly dependent on the concentration of initial solutions. Therefore, the glauconite could be used to extract a number of trace element ions weak solutions derived from the wastes of hydrometallurgical plants.

CONCLUSION

It has been established that the mechanochemical modification of glauconite sand by the addition of acidic salt NaH_2PO_4 promotes a significant increase in the sorption capacity of ions, *viz.*, of microelements for fertilizers. The sorption capacity increases with increasing the content of the acid salt and depends poorly on the concentration of initial solutions for the ions extraction, which allows using diluted solution for practical purposes. It has been demonstrated that the thermal treatment of glauconite sand and of samples on its ground results in impairing to a great extent the sorption properties of the sorption materials obtained. Using the methods of XRF phase analysis and thermal analysis structural and phase glauconite transformations revealed both in the course of the mechanical activation and thermal annealing thereof.

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