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Structural Development of the Mineral Sapropel Part upon Preparation of Carbon-Mineral Composites Therefrom*

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Abstract

Sapropels and carbon-mineral composites obtained by thermal treatment of sapropel at various temperatures were studied by X-ray phase analysis (XPA), transmission electron microscopy (TEM), BET and small angle X-ray scattering (SAXS) methods. It was found that the mineral phase in sapropels formed both elongated layered sapropels particles with fractal dimensions and compact large quartz particles. It was demonstrated that heating sapropels at 300 °C led to dispersion and stratification of mineral particles in sapropels, but herewith, the organic phase blocked up the pores formed and hinders an increase in the specific surface of the composite obtained. An increase in heating temperature to 600 °C leads to freeing the porous space from the carbon phase and increasing the total specific surface. A further increase in heating temperature to 900 °C gives partial sintering of the mineral phase and transitioning from fractal volumetric structures to surface ones, herewith, the value of the specific surface of composition materials almost does not change.

Key words: sapropel, carbon-mineral composites, SAXS, contrasting, dispersity of particles

INTRODUCTION

Natural bioresources (peats, sapropels, rice husk, *etc.*) are of great interest for use as inexpensive and available raw materials to produce various carbon and carbon-mineral multifunctional porous materials [1–5]. One of the considerable obstacles in the route of mass production and applications of such materials with specified porous characteristics is a relatively complex composition and often the absence of any data regarding the structure and dispersity of mineral particles that are ready templates in the composites obtained and can significantly affect the development of their porous structures. It is obvious that great difficulties arise in this case for reproducible preparation of the desired materials with constant properties in the industrial scale. To solve this technological tack studying the genesis of transformation processes both the in organic and mineral parts of biomaterials in processes of their thermal treatment is required. Unfortunately, these effects can overlap and difficulties with interpretation of the effects observed arise, since traditional research methods (for example, BET) do not allow studying them separately from each other. At the same time, applying new research methods (small-angle scattering using contrasting)

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allowed making substantive progress in understanding the nature of the occurring processes on the example of carbon-mineral composites obtained at thermal treatment of rice husk [6, 7].

An exploration of the nature of similar transformations of the organic and mineral phases when preparing carbon-mineral composites from sapropel is of interest. Sapropels that are bottom sediments of freshwater lakes also contain the organic and mineral phases and can be promising raw materials to prepare porous functional materials [2, 3, 5]. The reserves of sapropels in Russia are assessed in tens of billions of tons, moreover, this resource, unlike oil or gas, is renewable [2].

As demonstrated in our previous works, thermal treatment of sapropels leads to the formation of carbon-mineral porous systems, but the mechanism of developing the porous structure of carbon-mineral composites remains behind the scenes, there is no information regarding the structure and dispersity of mineral particles in a carbon matrix, there are only implicit data of possible effects of the mineral phase on the porosity of the material obtained [2, 3, 5, 8, 9].

Therefore, the goal of the present work is studying the genesis of the mineral phase of sapropels when preparing carbon-mineral composites from it by thermal treatment at various temperatures.

EXPERIMENTAL

Small-angle X-ray scattering

Measurements were made using Hecus S3-MICRO small-angle diffractometer (CuK_α, 50 W) with point collimation of the beam. The wave vector h (defined as $h = 4\pi\sin\theta/\lambda$, where 2θ is angle of dispersion; λ is wavelength of radiation of 1.541 Å) was measured in a range of 0.01 Å$^{-1} < h < 0.6$ Å^{-1}.

All shoutings were carried out in quartz capillaries with a diameter of 1.5 mm.

To obtain a selective signal from the mineral part of composites the contrasting technique consisting in impregnation of samples with a liquid with appropriate densities to mask additional scattering from the organic and/or carbon phases was used. The technique is described in more details in works [10, 11].

The programme packages ATSAS [12] and SAS Analyzer were used for data processing of small angle X-ray scattering (SAXS) [13]. Additionally, radius of inertia of particles according to the slope of the low-angle curve in (ln $(I(h)$; h^2) coordinates and the radius of inertia of the thickness of particles ($R_{G(\text{thick})}$) according to according to the slope of the low-angle curve in (ln $(I(h)h^2)$; h^2) coordinates were determined [14].

X-ray diffractometry

Diffraction measurements of sapropels were carried out using a ARLX'TRA diffractometer (Thermo Fisher Scientific) using CuK_α radiation (wavelength of 1.5418 Å). Measurement were made in the range of angles 10–90° in steps of 0.05°. The measurement time in point is 5 s.

True density measurement

True density determination of samples was carried out using an Accupus-1330 helium pycnometer (Micromeritics Instrument Corp.).

Specific surface determination

The determination of texture characteristics of samples was carried out according to physical adsorption of N_2 at a temperature of liquid nitrogen using an ASAP-2400 automated volumetric adsorption analyzer (Micromeritics Instrument Corp.).

Transmission electron microscopy

High resolution transmission electron microscopy (HRTEM) images were produced using a JEM-2010 device with the maximum resolution by lattice of 0.14 nm and an accelerating voltage of 200 kV. Samples for analysis were prepared by ultrasound dispersion in ethanol followed by suspension application to a special copper grid covered with carbon.

Preparation of carbon-mineral composites

Sapropel extracted from Gor'koye Lake (Omsk Region) and carbon-mineral composites prepared from this sapropel during its carbonization in a flow of argon at temperatures of 300, 600 and 900 °C were investigated in this work. The ageing time of sapropel at a specified temperature was 30 min. The original sapropel was subjected to preliminary drying in air at a temperature of 110 °C. The ash residue of the sapropel contained predominantly compounds of silicon (63.4 %) and aluminium (10 %). Compounds of iron (2.4 %), calcium (4.2 %), sulphur (2.1 %), potassium (0.6 %) and phosphorus (0.1 %) were also present as impurities.

RESULTS AND DISCUSSION

The diffractogram of the original sapropel is presented in Fig. 1. As can be seen from the data obtained, a large number of reflexes are observed in it. Such compounds as α-quartz (SiO_2), albite ($NaAlSi_3O_8$), muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$), leucite ($K[AlSi_2O_6]$) and hematite ($Fe_2O_3$) were determined among them. To identify the phases observed the RRUFF database on minerals was used [15]. As a whole, a similar composition is typical for sapropels [3]. Herewith, the reflexes referring to the quartz structure have high intensities, which complicates the determination of the remaining possible phases of aluminosilicates. Particle sizes of quartz were assessed using the Scherrer formula. The resulting value of particle sizes was 90 nm.

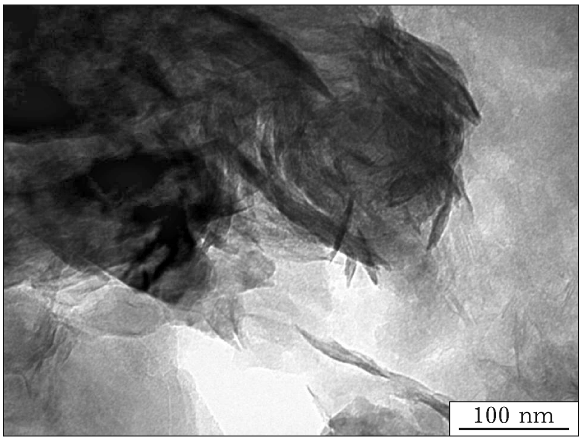

Fig. 2. TEM image of the initial sapropel.

According to TEM data, aluminosilicates particles in sapropels represent elongated particles with typical length values in a range from 20 to 70 nm and thickness in a range from 2 to 15 nm, respectively (Fig. 2). Herewith, an average value of length/thickness was 7.5. As can be seen in images (see Fig. 2), particles have a layered morphology, which agree well with X-ray diffractometry data, according to which layered aluminosilicates (muscovite) are present in

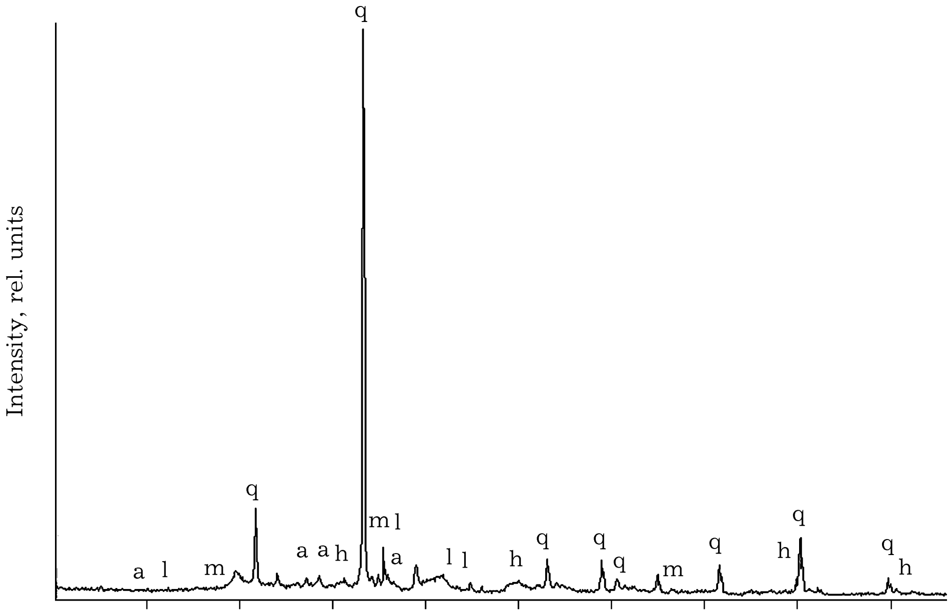

Fig. 1. Diffractogram for the initial sapropel. The Latin letters a, h, q, l, m denote the positions of the reflexes of albite, hematite, quartz, leucite and muscovite, respectively.

TABLE 1

Designations of carbon-mineral composites prepared from sapropels, their preparation conditions and characteristics

Samples	Preparation conditions	Ash content, %	Specific surface, m^2/g	True density, g/cm^3
Initial sapropel, SP 110	Air drying at 110 °C	64.3	3.3	2.288
SP 300	Heating in argon at 300 °C, 30 min	74.8	5.6	2.507
SP 600	Heating in argon at 600 °C, 30 min	88.4	49.1	2.672
SP 900	Heating in argon at 900 °C, 30 min	94.2	44.0	2.797

the sapropel composition. Additionally, and larger quartz particles that have a relatively compact shape and dimensions in a range from 100 to 500 nm can also be seen in TEM images.

Further, the original sapropel was subjected to thermal treatment in a flow of argon at various temperatures (Table 1). As can be seen from the data obtained, carbonization of sapropel leads to the preparation of carbon-mineral composites from it. It is interesting to note that a significant increase of the specific surface begins only at relatively high treatment temperatures (600 °C) and the achieved value of the specific surface almost does not change at an increase in the temperature of thermal treatment to 900 °C. Such processes as carbonization of organic parts in sapropel with the formation of a developed carbon surface, and also transformation of sapropel mineral compounds can happen during thermal treatment.

The MD-SAXS method was used to analyse the occurring structural changes. It is important to note that the space resolution by large particles in the current configuration of a small-angle diffractometer is limited by a value of approximately 65 nm, therefore, quartz particles will not make contribution to the observed signal of small-angle scattering and the particles sizes of the observed scattering will be limited by a value of 65 nm. But in this case this is

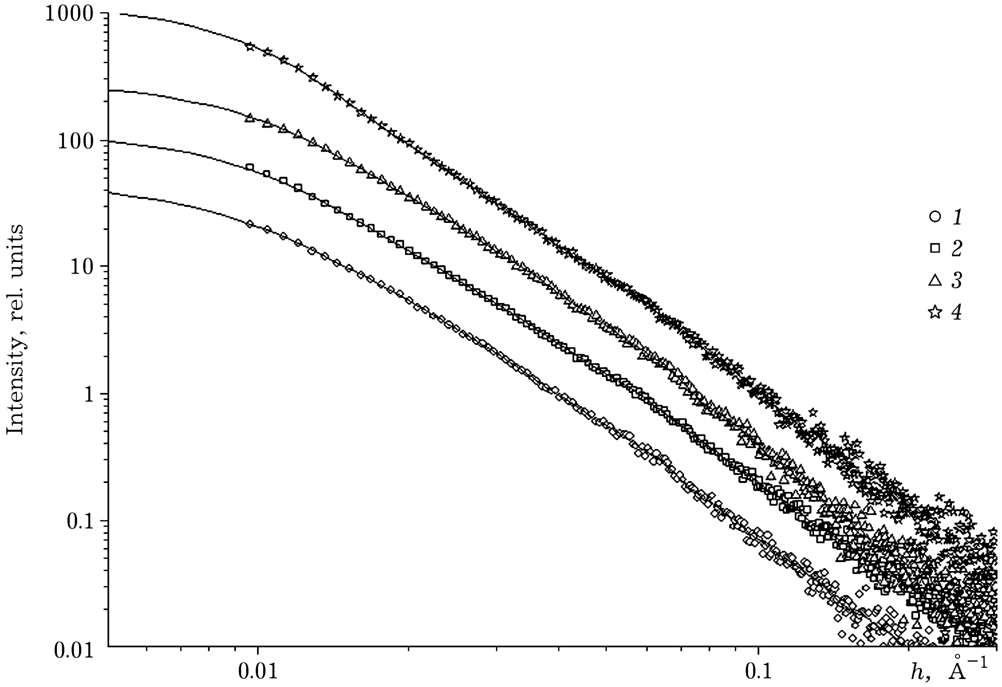

Fig. 3. SAXS curves for initial samples of sapropel SP 110 (*1*) and carbon-mineral composites: SP 300 (*2*), SP 600 (*3*), SP 900 (*4*).

TABLE 2

Structural characteristics of the studied carbon-mineral composites

Samples	Degree of slope of the SAXS curve	Fractal dimension	R_G, nm	$R_{G(\text{thick})}$, nm	Thickness, nm
SP 110	3.0	3.0	16.7±0.5	1.8±0.3	6.2
SP 300	2.9	2.9	16.4±0.6	2.0±0.3	6.9
SP 600	3.1	3.1	16.1±0.9	2.0±0.3	6.9
SP 900	3.6	2.4	16.9±0.7	4.3±0.4	14.9

not so much substantial, since particles with the sizes of 100 nm and more weakly affect the values of the specific surface of the tested materials. Also, quartz particles are very stable under these conditions of heat treatment; therefore, they are inherently just ballast in the composition materials obtained.

Figure 3 presents SAXS curves for sapropel and carbon-mineral composites based on it, they are in a range of large values of h are usually approximated by a power function of the type $I(h) \sim h^{-x}$, where x is the degree of downturn of the SAXS curve that can be useful at analysis of the morphology of particles [14]. As can be seen from the data of Table 2, samples represent the dispersed phase of an uncertain morphology, since the degree of downturn of SAXS curves is found in the range of values from 2.9 to 3.6. This range of values of the degrees of downturn from 2.0 to 4.0 can relate to aggregates with fractal and/or elongated structures. Herewith, the exponents of the degree of downturn of the SAXS curve in the range of 2.0 to 3.0 is generally attributed to the volumetric fractals, and from 3.0 to 4.0 for surface fractals [16, 17]. The value of the degree of downturn equal to 4.0 refers to compact, smooth particles. The fractal dimension value in this case is determined as $x = D$ for volumetric fractals and $x = 6 - D$ for surface fractals (x is apparent exponent of downturn of the SAXS curve, D is fractal dimension).

As can be seen from the data, the fractal dimension value of particles slightly varies depending on calcination time up to 600 °C inclusive (see Table 2). At calcination time of 900 °C, apparently, sintering begins, and fractal particles begin to transform into particles of more compact morphology. The radii of inertia of particles (R_G) and the radii of inertia of the particles thickness were determined from the data of SAXS obtained ($R_{G(\text{thick})}$) [14]. These parameters characterize the average sizes of particles, moreover, the latter parameter is observed in cases of pronounced particle anisometry, which agrees well with the availability of elongated particles, according to TEM data (see Fig. 2). A meaningful increase in a value of the radius of inertia of particle thickness is observed only at sapropel treatment at a temperature of 900 °C. Therefore, the value of R_G depends not only on the particle sizes but also on its shape, then knowing the shape of particles a priori, one can compare SAXS data with TEM data. Thus, according to calculations, in case of using particles of a solid triaxial ellipsoid as the form factor, a value of $R_G = 16.8$ nm corresponds to an elongated ellipsoidal particle with the lengths of semi-axes of $a = 5$ nm, $b = 5$ nm, $c = 37$ nm, respectively [18]. As can be seen, the obtained dimensions agree well with the TEM data obtained earlier.

It is also possible to determine the sickness of the ablated particles (T) from a value of the radius of inertion of thickness under condition of particle homogeneity. According to [14], ${R_{G(\text{thick})}}^2 = T^2/12$, where T is particles thickness. Since in our case, particles are deliberately inhomogeneous and have a certain fractality, this expression can be used only as an approximate assessment of particles thickness. Although when comparing of the average thicknesses obtained according to SAXS data with TEM data (thicknesses from 2 to 15 nm) qualitative data consent is observed (see Table 2).

Nevertheless, as can be seen from the data obtained significant changes in the dimensions of sapropel particles and carbon-mineral composites were not found.

It is likely the occurring processes of carbonization of the organic phase and possible transformations of the organic phase compensate each other and according to SAXS data, only weak differences are observed, except for SP 900 sample, where a decrease in particles thicknesses is obviously driven by their sintering. Therefore, for more detailed analysis of the changes of mineral phase dispersity in sapropel, the contrast enhancement method was used [10, 11]. The averaged density of the carbon-containing phase was assessed using the values of true density of samples and the proportion of the mineral phase in them (see Table 1). Herewith, an assumption was introduced that the samples contained only two phases (organic and mineral) with different densities. The averaged density value for the carbon-containing phase was (1.35±0.1) g/cm^3. By knowing this value, the samples were contrasted by a liquid with the corresponding density to mask the signal of the carbon-containing phase and selective receiving signals from the mineral phase. Figure 4 presents SAXS data for the investigated samples using masking fluid.

As can be seen from the data, the scattering strength of the contrasted samples is naturally reduced in comparison with initial data. But in this case, the scattering signal refers to only the mineral part of composites and it can be seen that in comparison with initial data, the form of SAXS curves substantially changes (see Figs. 3 and 4). Attention should be drawn that when comparing SAXS data for the initial samples and after using the contrast enhancement method, the R_G value changes relatively little, while a substantial decrease in $R_{G(\text{thick})}$ value is observed in case of contrasting.

This testifies that the organic and/or carbon phase unite mineral phase particles into a single particle by increasing in such a manner their thickness. When contrasting such a composite aggregate is observed already as a set of individual thinner mineral blocks. As can be seen from Table 3, the most noticeable differences are observed for a carbon-mineral composite sample obtained at 300 °C. The values of R_G and $R_{G(\text{thick})}$ after calcination of sapropel at T = 300 °C decrease, and a further increase in treatment temperature up to T = 300 °C, correspondingly, lead to a gradual increase in these parameters. It is interesting to note that the radius of particles thickness (more than in two times)

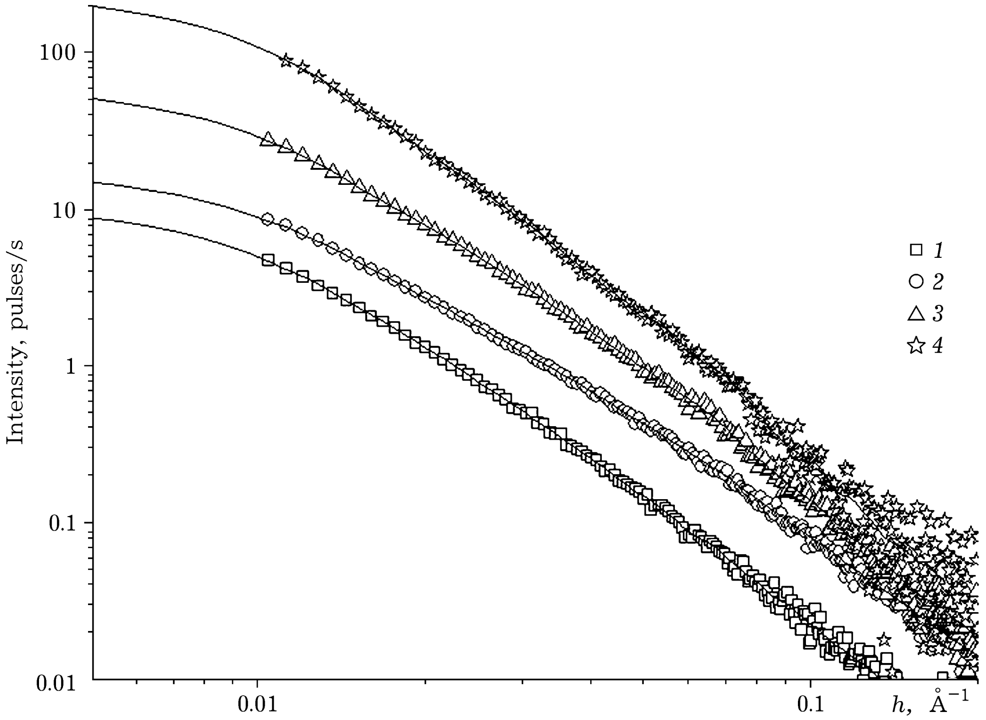

Fig. 4. SAXS curves for sapropel samples and carbon-mineral composites when using the contrast enhancement method: SP 110 (*1*), SP 300 (*2*), SP 600 (*3*), SP 900 (*4*).

TABLE 3

Structural characteristics of the mineral part of carbon-mineral composites samples after contrasting

Samples	Degree of slope of the SAXS curve	Fractal dimension	R_G, nm	$R_{G(thick)}$, nm	Thickness, nm
SP 110	2.9	2.9	16.2±0.5	1.5±0.3	5.2
SP 300	2.4	2.4	15.0±0.6	0.6±0.2	2.1
SP 600	3.0	3.0	15.6±0.7	1.2±0.2	4.2
SP 900	3.6	2.4*	16.4±0.6	2.8±0.4	9.7

*Surface fractal.

decreases most substantially at a small decrease in the inertion radius. This testifies a decrease in particles thickness at approximate preserving the remaining sizes, that is splitting of plane mineral particles into even finer fragments occurs. Since there are layered aluminosilicates in the sapropel composition, their splitting into finer particles at an increase in temperature is basically quite a natural process. This is indirectly confirmed and by the fact that a decrease in values of the downturn degree of the SAXS curve is observed at thermal treatment of sapropels at $T = 300$ °C, which leads to a change in the frontal particle dimensionality from 3.0 to 2.4 (see Table 3). If splitting of particles onto finer layers occurs, it is reasonable to expect that fractality (atomism) of such a system will only strengthen, which is demonstrated by the obtainable dimensionality value. A further increase in treatment temperature leads to a gradual decrease in fractality that is sintering of particles with the formation of more compact structures occurs. Based on these data, one can propose genesis of conversion of sapropel at its thermal treatment at various temperatures.

The assumed scheme of conversions of sapropel is given in Fig. 5. Apparently, partial splitting of layered particles occurs at $T = 300$ °C, which according to SAXS data, is expressed as a change in particles fractality and a decrease in their dimensions, especially, thickness (see Table 3). Earlier, when analysing sapropel samples by thermogravimetry methods a decrease in the sample mass in a range of temperatures of 280–400 °C was demonstrated [3, 5]. Although these changes were explained primarily by carbonization of organic matter in sapropel, one cannot exclude and partial isolating crystallohydrate water from aluminosilicates and splitting of mineral phase particles due to the gas formed. Thus, the temperature range of decomposition is relatively wide, and partial decomposition was in fact observed for some samples at temperatures of the order of 300–400 °C [19, 20]. Therefore, splitting of muscovite particles is quite possible in our case. Nevertheless, at such significant transformations of the mineral part of particles, an increase in the specific surface of samples as a whole does not happen (see Table 3). Apparently, the organic

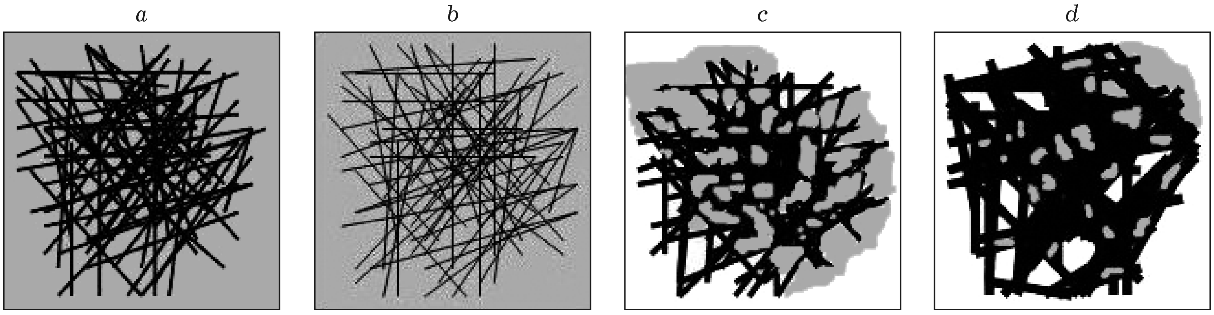

Fig. 5. Scheme of transformation of sapropel at various heat treatments. The black colour indicates the mineral part, grey – organic and carbon: *a* – initial sapropel, *b*–*d* – treated at a temperature of 300, 600, and 900 °C, respectively.

part of composites, which does not form the stable carbon phase at this temperature, prevents this, and can be found in the thermoplastic condition [21]. Herewith, this mass fills is the pores formed, and therefore, an increase in the material specific surface does not happen. At an increase in treatment temperature of sapropels to $T = 600$ °C, according to SAXS data, partial particle sintering already begins, *i. e.*, the thin plates formed at low-temperature heating begin to aggregate again with each other, which leads to an increase in sizes of mineral phase particles. But since heating of sapropel at $T = 600$ °C already leads to a substantial increase in the specific surface of the sample, as a whole, one can assume that the carbon part of the particle begins to form its own porous structure and/or a partial liberation of the porous space of the mineral part of the composite early formed occurs. An observed decrease in the proportion of the carbon phase at an increase in heating temperature and additional sintering of the mineral phase at a further increase in calcination temperature to 900 °C testify in favour of the second option. Apparently, liberating of pores from the carbon phase can compensate for the observed sintering of the mineral phase, since the specific value of the sample surface at $T = 900$ °C almost does not differ from the previous stage at $T = 600$ °C (see Table 3). Also, at the calcination stage at $T = 900$ °C a transition of volumetric fractal – surface fractal consisting in sintering of the initial fractal structure with the formation of more compact particles that herewith have only the rough surface (surface fractal) occurs.

CONCLUSION

Sapropel and carbon-mineral composites obtained from therefrom upon its thermal treatment at various temperatures were studied by the complex of physicochemical methods (XPA, TEM, BET and SAXS). It was found that the sapropel mineral part in consisted of large quartz particles of the compact shape with the sizes of 100–500 nm and finer anisometric aluminosilicates particles with a typical length from 20 to 70 nm and a wideness 2 to 15 nm, respectively, herewith, having the fractal dimension. It was demonstrated that precisely layered aluminosilicates played the major part in the formation of the pore structure of carbon-mineral composites prepared from sapropel. It was discovered that thermal treatment of sapropel at 300 °Cled to dispersion and stratification of mineral particles due to the partial removal of water of crystallized water, herewith, the organic phase blocks the pores formed in the composite structure and prevents an increase in the specific surface of the sample, as a whole. At a further increase in heating temperature of sapropel to 900 °C, sintering of the mineral phase happens and a transition from volumetric fractal structures to surface ones occurs due to the formation of compact particles with the rough surface from initial fractals. An increase in temperature leads to the further removal of the carbon phase from composites, which compensates sintering of mineral particles at 900 °C, and herewith a substantial decrease in the material specific surface does not happen.

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