

MINERALOGICAL IDENTIFICATION OF MACROCOMPONENTS OF INORGANIC PART OF KANSK-ACHINSK COALS

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The results of research of mineral formation in composition of coal samples with different ash level using expanded complex of physical chemical methods allowing increase of reliability of revealing ash-forming components in coal to estimate variants of their transformation as applied to techniques of coal preparation and burning, interaction with gaseous products of these techniques are presented.

Introduction

Mineral products of coal burning have a various impact on the work of boiler installation: decreasing heat of heating surface, making abrasive wear of gas path elements, influencing the efficiency of gas cleaning and reliability of ash-and-cinder removing. Character and degree of these properties depend on the composition of inorganic coal fraction decisively.

To simplify the characteristic of bonds with organic substance coal inorganic part is conventionally divided into internal and external constituents. The external constituent is presented as a system of mechanic impurities that are separated into separate particles at coal breakage and, therefore, easily isolated by physical methods. In terms of comparative availability of external constituents to isolate carbon dust it was they that became the subject of majority investigations of initial mineral part of Kansk-Achinsk coals (KAC). As a result the main mineralogical forms have been revealed, quantitative estimations of some of them have been made. These results are suitable for applied problems of predicting and simulating the processes as applied to different techniques of fuel-burning. Besides, they are fragmentary since they are mostly obtained either by single coal sample or on the basis of not very effective methods often at sufficient difference in methodical equipment.

In this connection, the study of composition and properties of mineral part of such important for energy supply coals as KAC is urgent in the aspect of increasing reliability due to application of complex of modern methods and presentation of the samples involved in the range of ash level.

Methods of research

Developing applied aspect – impact of mineral part of coals on the operation of steam boilers is appropriate to pay attention, first of all, to inorganic macrocomponents presenting the basis of ash forming in coal burning. According to coal-chemical classification [1], Si, Al, Fe, Ca, Mg, Na, K, S, Ti are referred to them. Research of initial mineralogical forms was carried out on the fractions of more than 1600 kg/m³ density isolated from KAC analytical samples of different deposits.

To characterise the element distribution in coal structure and to set the range of density of isolated fraction groups providing the most complete differentiation of mineral substances electron-probe analysis using CAMEBAX installation was applied. Element concentration was defined by the results of scanning in two mutually perpendicular directions in the plane of polished section prepared on two samples investigated [2]. As standards natural minerals including quartz, feldspar, tiff, albite, anorthite, orthoclase, and pyrite were used.

To isolate external mineral components coal samples were preliminarily comminuted in laboratory non-aerated mill providing practically equal fineness of grinding ($R_{200}=1...3\%$, $R_{90}=10...15\%$, $R_{40}=45...55\%$). Fractionation in density was made in laboratory centrifuge at 3000 rev/min with determination of lighter particles at first ($\rho \leq 1400$ kg/m³) and isolation from the rest of fractions of 1600...2280, 2280...2860, >2860 kg/m³ density. The coal samples of different deposits in the range of ash level of dry state $A^d=5,1...20,1\%$ were subjected to separation into fractions.

Macrocomponent composition of the fractions is defined by means of the methods of chemical silicate analysis [3]. Crystal compounds were investigated by the method of roentgen-phase analysis (RPA) applying native diffractometers with different anode material of roentgen tube. Diffractograms were processed by means of the tables of interplanar spacing [4] and roentgen mineral tables [5–9]. If one needed to define more accurately the composition the method of derivatography (DTA) or its constituents (thermography, gravimetry) using derivatograph ОД-102 of «Metrimplex». For the purpose of diagnostics of silicates referring to the class of minerals with a wide variety of crystal structures with close values of atomic dispersion factor and, therefore, hard to identify by roentgen methods Infrared spectrometry was used. IR-spectra were read by spectrophotometer UR-20 of «Karl Zeis-Iena».

Element distribution in coal

Variety of spectra of characteristic radiation obtained at electron-probe scanning of KAC samples are presented in fig. 1. The value of intensity of reflexes at graphical image of their appearance along the line

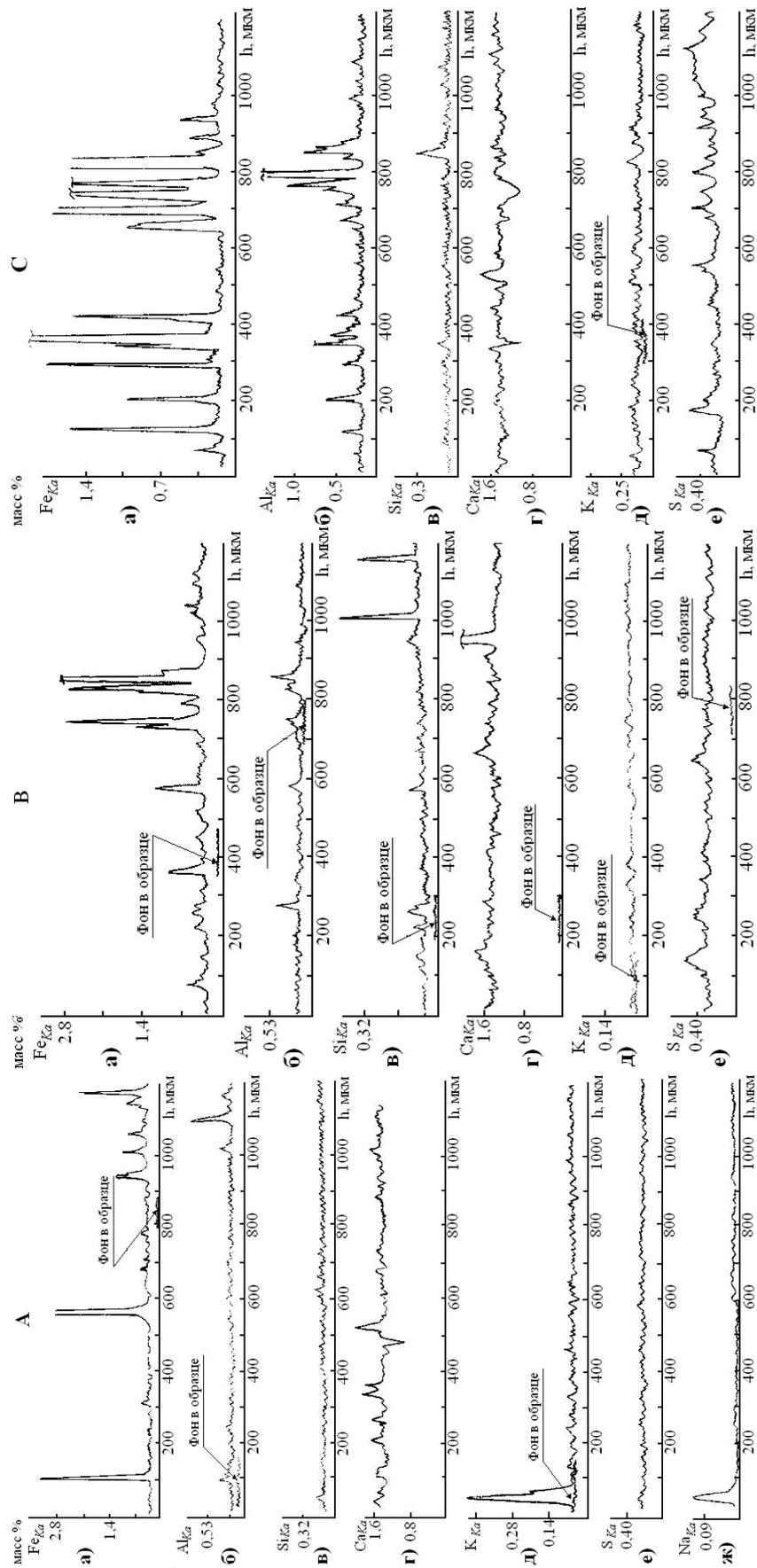


Fig. 1. Typical dependences of characteristic K α -radiation of elements on the line length of scanning: а) Fe; б) Al; в) Si; г) Ca; д) K; е) S; ж) Na; з) Al; и) Na; л) K; м) S; н) Fe; о) Al; п) Si; р) Ca; с) K; т) S; и) Na; к) Na; л) K; м) S.

length of scanning is presented in units of concentration expressed in mass % and calculated from the equation:

$$C = C_0 \cdot \frac{I}{I_0} \cdot 100 \cdot \alpha,$$

where I and I_0 – intensities of characteristic radiation corrected by the value of sample and standard hum obtained in the same conditions of shooting, C and C_0 – concentrations of elements in the sample and standard composition, but α – coefficient including absorption of characteristic KK_α -radiation owing to «matrix» effect [2]. Using complex metals as standards in the aggregate close to ash in chemical composition permitted to consider $\alpha \sim 1$.

Statistic distribution of diffraction maximums of characteristic $Fe_{K\alpha}$ -radiation (fig. 1, a) reveals some mineral formations. Superposition of radiation maximums on Fe and S corresponds to pyrite (FeS_2), but peak on Fe without corresponding peak on S – siderite ($FeCO_3$). Besides, intensity of $Fe_{K\alpha}$ -radiation along scanning line is characterised by high value ($\sim 0,15...0,20$ mass %) above the level of background $Fe_{K\alpha}$ in the sample. It points out that apart from the mentioned minerals iron is present as a component of organomineral compounds. As a kind of such components up to $0,2...0,3$ mass % of S, $\leq 1,5...2,5$ mass % of Ca, $0,005...0,1$ mass % of K, $\leq 0,05...0,07$ mass % of Al, as well as that of Na are also defined. Noticeable part of external mineral formations is formed by silicate and silica-alumina forms including quartz (α - SiO_2) and various clay minerals.

The density of diffraction minimums P_i , the intensity of which changes synchronously along scanning line can be taken as one of factors characterising composition of minerals in coal structure. It is defined by calculation according to the equation:

$$P_i = \frac{\sum B_i}{L},$$

where B_i – half-width of reflexes of i -element (numerically equal to the reflex width at the half of its height), L – length of scanning line. Statistic analysis of density of diffraction maximum distribution, responding to mineral compositions permits to suggest that in the process of preparation of coal powder (grinding <200 mkm) to obtain purely coal particles is impossible.

It is confirmed by the conclusion drawn earlier on the basis of studying the degree of genetic varieties distribution of coal mineral part at non-aerated grinding and used as a basis of classification of powdered-coal particles [10]. Even at the highest degree of coal grinding there are inorganic components as a specific organomineral matrix in the composition of a separate particle. One can discuss only purely theoretical possibility to isolate ash-free coal particle in the class of superfine particles. Calculations as applied to commercial powder of KAC with ash-level in the dry state of $4...6$ mass % show [11] that beginning from the particle size of the order of $5...15$ mkm there appear inclusions of proper minerals in organomineral matrix which are changed from monomineral to polymineral particles as the size of the particles increase up to 30 mkm.

Mineralogical composition

Chemical composition of ash mass without sulphates (mass %) of coal fractions with density:

- More than 2860 kg/m^3 : $0,5...29,1$ % SiO_2 ; $50,8...97,0$ % Fe_2O_3 ; $2,5...26,3$ % $Al_2O_3+TiO_2$; $0,0...9,1$ % CaO ; $0,0...4,1$ % MgO ; $0,4...0,7$ % Na_2O+K_2O ;
- $2280...2860 \text{ kg/m}^3$: $73,5...90,7$ % SiO_2 ; $0,3...9,1$ % Fe_2O_3 ; $3,3...23,9$ % $Al_2O_3+TiO_2$; $0,1...8,1$ % CaO ; $0,0...1,6$ % MgO ; $0,8...2,5$ % Na_2O+K_2O .

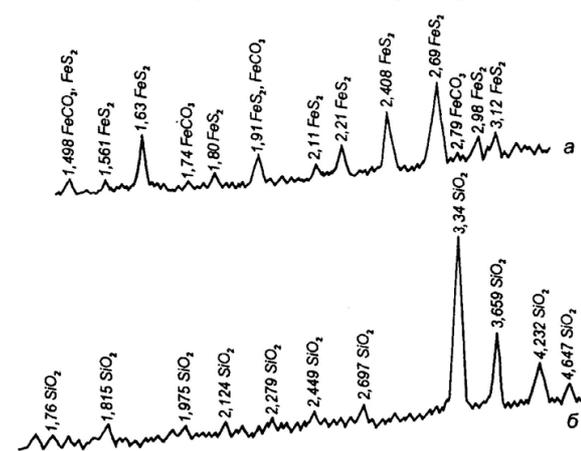


Fig. 2. Typical roentgen diffractograms of coal fractions of the density: a) >2860 ; b) $2280...2860 \text{ kg/m}^3$

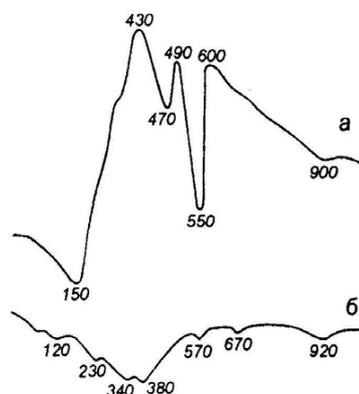


Fig. 3. Thermograms of fractions $\rho > 2860 \text{ kg/m}^3$ (a) and its ashes (b) in air (shooting mode: 10°C/min ; $DTA = 1/5$)

In the ash of fractions $\rho > 2860 \text{ kg/m}^3$ iron oxides prevail. Roentgen-phase analysis (fig. 2, a) shows that mineralogical base of the fraction is iron disulfide with the structure of pyrite and marcasite (diffraction effects at interplanar spacing $d/n=3,12; 2,98; 2,69; 2,408; 2,21; 1,91; 1,63$ etc.), with impurity of siderite $FeCO_3$ ($d/n=69; 2,12; 1,74; 1,498$). Thermography of the fraction proves the presence of these minerals and coincides with the data [12] about the fact that in the presence of coal impurities FeS_2 reactions occur at the temperature $100...150^\circ \text{C}$ lower in comparison with the reactions of pure pyrite (thermal effects at $470, 490, 550^\circ \text{C}$ in fig. 3, a). Exoeffect at 600°C is a reflection of secondary oxidation of ferrous oxide up to Fe_2O_3 (with the increase of weight), which is proved by endothermal polymorphous transformation of haematite (without change

of weight) in thermogram fig. 3, *б*. Thermal analytical effects of siderite are hidden by deeper pyrite peaks. One also points out the presence of quartz (the order of 5 %) on the effect of polymorphous transformation (at 570 °C in fig. 3, *б*), as well as insignificant number of carbonates of CaCO₃ type, which is proved by weak endothermal bends of thermograms at 900 and 920 °C.

The fraction 2280...2860 kg/m³ concentrates in itself the most part of SiO₂ coal, but the second macrocomponent in size is Al₂O₃ – from 3 to 24 %. Numerous roentgen-phase analytic investigations of this fraction show the presence of α -quartz with high degree of resolution of diffraction picture. Typical diffractogram of the fraction (fig. 2, *б*) contains only characteristic effects of reflection α -SiO₂ ($d/n=4,647; 3,659; 3,34; 2,697; 2,449$ etc.). Stable intensity of the main quartz reflection does not reveal the products of three-phase reactions with quartz after continuous exposure of the fraction at temperatures 400 and 800 °C as well as the absence of new effects; it indicates a large number of clay materials. Nevertheless, fraction roentgenograms in the area of small reflection angles permit to detect the presence of weak-crystallized compounds, which can for good reason be explained by the diffraction of beams from mixed and irregularly interstratified structures, typical for clay minerals [9]. As a result of special shooting of diffractograms at small reflection angles (fig. 4) diffraction effects of average intensity in the range of interplanar spacing $d/n=8,56...6,51$ and low intensity at $d/n=3,56$, that correspond to just several clay minerals: kaolin, dickite, nacrite are formed. Besides, diffractograms contain very weak reflections at $d/n=9,1...10,1$, which are noted as characteristic for other clays of silicates and minerals: illite, montmorillonite, pyrophyllite, mica, talc [7, 9, 13]. Thermal analytical curves of the fraction (fig. 5) isolated from coals with different ash level is characterised by identical thermal effects. At 120...160 °C liberation of moisture takes place; the following the most significant exothermal effect results from oxidation of organic substances and is intensified by carbonate formation. The effects of the latter appear at 460...470 °C and 900...930 °C. The most clearly defined effect is 570...575 °C corresponding to polyforming (α - β) quartz transformation. Comparison of the given effects when heating and cooling the probe based on reversibility of quartz lattice reconstruction shows that at heating (especially that of Nazarovsk coal) its value is more than at cooling. It provides the grounding for the conclusion on the fact that effect at heating is intensified owing to superposition of endothermal effect of clay mineral dehydration, which is confirmed by the presence of exothermal effects at 980...1000 °C for the probes, which have the most significant effects at 570...575 °C (fig. 5, *б*). According to the data [13], kaolin dehydrates in the range of 550...700 °C, but metakaolin forming after it and presenting a tight association of silica losses crystal lattice at 980...1000 °C, which is demonstrated by positive thermal analytical effect of amorphisation.

On the IR-spectrum of absorption in the long-wave area (fig. 6) the fraction is characterised by a more complex composition. Using the method of spectra compa-

risson revealed by the previous analysis of minerals as well as the other close-in-structure materials one can identify α -quartz and kaolin. According to the data [14] IR-spectrum of pure α -quartz contains intensive band in the range of frequencies 1200...1100 cm⁻¹, strong bands about 530 and 460 cm⁻¹ referring to valent and deformative fluctuations of silica-oxygen frame tetrahedrons (O-Si-O и Si-O-Si), as well as sufficiently strong band of doublet in the range of 830...750 cm⁻¹, referring to fluctuation (Si-O-Si) of rings from SiO₄. Distinctive bands of kaolin in the long-wave part of IR-spectrum are developed at the frequencies: 1121, 1031, 939, 916, 797, 786 cm⁻¹ according to [15].

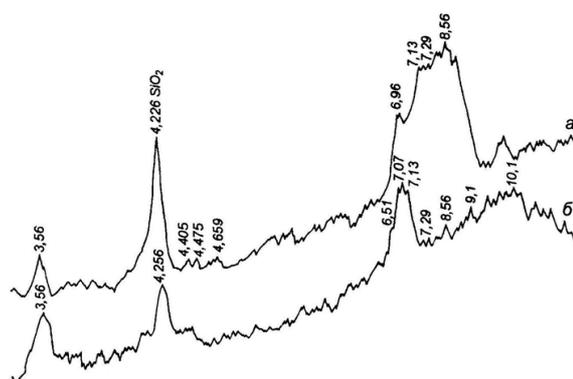


Fig. 4. Roentgen diffractograms of the fractions of 2280...2860 kg/m³ density in the area of small reflection angles: a) Nazarovskiy; б) Uryupskiy coal

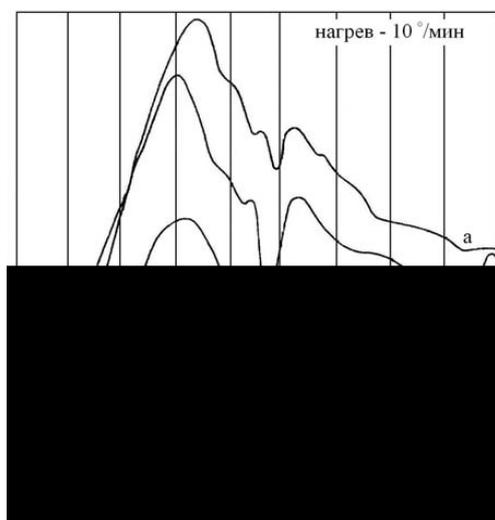


Fig. 5. Thermograms of fraction 2280...2860 kg/m³ in nitrogen media: a) Beryozovskiy coal, 5,65 %; б) Nazarovskiy coal, 9,50 %; в) Irsha-Borodinskiy coal, 13,16 %

Comparison of spectra of different mineralogical forms of silicate [14] allows for conclusion on the presence of other modifications apart from quartz. Thus, the change of absorption band in the range 830...750 cm⁻¹: instead of doublets peculiar to α -quartz, a united band is fixed (fig. 6, *a*), which is typical for tridymite, cristobalite, amorphous silica (appearance of the latter can be the result of long fine grinding for sample preparation [16]).

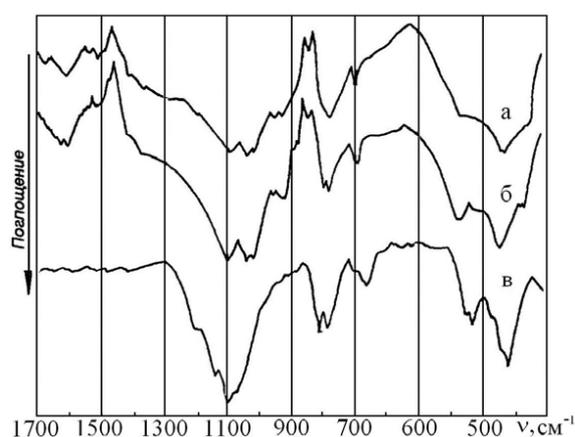


Fig. 6. Spectrum of absorption of fraction 2280...2860 kg/m³ in infrared region: a) Uryupskiy coal A^d=7,54 %; б) Nazarovskiy coal 9,42 %; B) α-quartz



Fig. 7. Roentgen diffractograms of coal fraction of 1600...2280 kg/m³ density

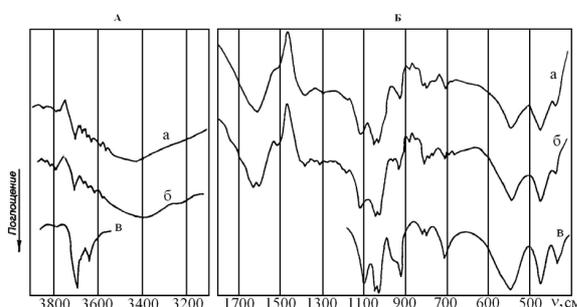


Fig. 8. IR-spectra of fraction absorption of 1600...2280 kg/m³ density: A – in short-wave and B – in long-wave part: a) Uryupskiy coal, A^d=7,54 %; б) Nazarovskiy coal, A^d=9,42 %; B) kaolin

Against the general background of kaolin (fig. 8, б) the signs of typical for stratified silica of isomorphous atom displacement (hydromica, montmorillonites etc.) are observed. It is, for example, expressed in changes of main bands of quartz absorption, change of clearness of spectrum due to disordered structure. Complex doublet of pure tetrasilicate ion is transformed into triplet in the range of 1209...900 cm⁻¹, where the main peak becomes the middle one. This change reflects the increase of displacement degree of silicon by aluminium in tetrahedral layers [14]. The same thing is reflected by the presence of band of 925 cm⁻¹ (AL-O-fluctuations), as well as broadening of the main absorption band. Besides, the

changes in the range reacting to ion displacement on octahedral layers typical for montmorillonite and muscovite: resolution of H-O-Al-fluctuations at the frequency 935 cm⁻¹ becomes worse due to decrease of Al³⁺ and decrease of intensity of band Si-O-Al-fluctuations at frequency 535 cm⁻¹ (fig. 6, a). Short-wave part of IR-spectrum of the given fraction reveals deflections in fluctuation bands of OH-groups showing similarity with monmorillonite, muscovite, phlogopite, and biotite.

Clay minerals in coals are distinguished by a great variety not only in structure and composition, but also in origin and forms of bonds with coal substance [17]. Isolated in the fraction composition 2280...2860 kg/m³ groups of clay minerals should be referred to terrigenous ones including epigene inclusions isolated in mechanically. Besides, there is both separate coal microlitotype – carbominerites representing coal-mineral concretions which are stably reported in KAC investigations and are often presented by carbhillite (concretions of coal with clay minerals, the part of which amounts from 20 to 60 %) [17].

Table. Identification of absorption bands of IR-spectra of 1600...2280 kg/m³ fraction

Frequency of absorption bands of IR-spectrum, cm ⁻¹	Characteristic frequency of absorption bands [14–16, 18]		
	Frequency, cm ⁻¹	Nature of fluctuations	
3700...3705	3705...3695	OH-groups of kaolin, phlogopite, biotite	
3670...3660	3670...3663	The same	
	3650	The same	
3635...3620	3635...3620	OH-groups of kaolin, montmorillonite, muscovite	
	1605	Deformative (H-O-H) of crystallization water	
1415...1390	1450...1410	CO ₂ of carbonates	
1110...1105	1200...1100	Valent (O-Si-O) of silica-oxygen tetrahedrals	
1035...1010	1100...900	Valent (Si-O) of silicates	
955...950	952	(Al-O) and (Al) of silicates in tetrahedral positions	
935...915	1000...800	(H-O-Al) of silicates	
	877	CO ₂ of carbonates	
	860	862...844	Silica-oxygen tetrahedrals (montmorillonite)
	790	830...750	Rings (Si-O-Si) of SiO ₄ groups of silica-oxygen tetrahedrals
800...700	800...500	(Si-O-Al) of silicates	
538...510	550...450	The same	
470	530...460	Deformative (Si-O)	
430	460...430	The same	

In terms of the enumerated peculiarities it seems to be appropriate to consider clay substance in the composition of fraction with the most probable presence of carbominerite. According to the data on genesis of coal mineral components [17] this mineral association with coal is related to the fraction 1600...2280 kg/m³. Chemical composition of ash sulphate-free mass of this fraction: 48,6...67,4 % SiO₂; 1,3...13,7 % Fe₂O₃; 10,7...34,5 % Al₂O₃+TiO₂; 2,5...22,0 % CaO; 0,9...3,20 % MgO; 0,8...2,2 % Na₂O+K₂O.

Roentgen-phase analysis identifies such crystal substances as quartz by the effect at $d/n=3,68; 3,34; 2,45; 2,28; 2,12$ etc.; there are also diffraction effects at small reflection angles indicating the presence of clay minerals (fig. 7).

IR-spectrometry confirms complex composition of the fraction (fig. 8). In table comparison of obtained absorption maximums with that identified in the works in frequency [14–16, 18] are presented by the nature of fluctuations and characteristic frequencies of specific atom groups of clay minerals. Their peculiarity is the presence of intensive bands of $400...600, 900...1100, 3400...3700 \text{ cm}^{-1}$ [17] in infrared spectra of absorption. One can see that IR-spectra obtained characterise inorganic part of the fraction as a clay substance on kaolin base with quartz, carbonate inclusions, which is typical for carbahillites.

In its turn, clay constituent contains along with proper kaolin dickite belonging to the same kaolin group as well as poorly differentiated (probably not-clearly crystallized) minerals with features of montmorillonite and illite (hydromica) groups. Such nature of clay substance can be explained by the property of metamorphism of laminated silicates [17].

Conclusion

Mineralogical composition of inorganic mass isolated from coal is presented by disulphites, quartz, and kaolin with impurities of siderite, tuff, and clay minerals of montmorillonite, hydromica, and feldspar type. Significant part of such ash-forming coal macrocomponents as calcium, magnesium, sulphur, iron, aluminium, potassium and sodium form organomineral

compounds. Among them special place is occupied by carbominerite concretion, in the basis of physico-chemical nature of which there is a property of clays to form absorption complexes of humic acids and organomineral compounds with crystal lattice explained by ability of laminated silicates to cation exchange. In the works on clay mineralogy it is pointed out that connecting fragments of humic substances with the surface of crystal lattice can be non-silicate forms of sesquioxides or polyvalent cations iron in particular.

Peculiarities of mineralogical characteristic of macrocomponents of KAC inorganic part allows for distinguishing the following main types of powder-coal particles depending on the degree of coal grinding:

- I – monomineral particles representing mineralogically homogeneous formation as a form of which quartz, pyrite, siderite, feldspars, kaolin, micas are mostly probable;
- II – organomineral particles (of the finest class) representing organic mass of coal with uniformly distributed inorganic components in it at the chemical level;
- III – particles representing absorption concretions of organomineral base (of type II) with clay minerals or their products of metamorphism;
- IV – particles representing mechanical concretion of organomineral base (of type II) with monomineral inclusions (of type I);
- V – concretions of organomineral base with mechanical polymineral inclusions of not less than two heterogeneous minerals (of the largest class of the particles).

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