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Definition of Slurry Component in Coal Enrichment and its Comparison with Structural Models

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Abstract. Ecological challenges of the XXI century make us seek ways to more fully use non-renewable resources, including coal. When coal is enriched, a considerable amount of unused slurry is accumulated, containing an organic component. Composition of coal slurry, generated during coal enrichment process, was investigated by elemental analysis, X-ray phase analysis and IR spectroscopy. Mineral and organic composition of coal slurry was studied in detail. The structural models of the basic elements of coal slurry were obtained.

1. Introduction

Coal is one of the main energy producing materials of organic origin, it is also a source of raw material for chemical industry. Structurally, coal is a complex highly-porous heterogeneous rock, consisting both of various organic and inorganic impurities. Chemically, coal is a mixture of high-molecular-weight polycyclic aromatic compounds [1], water, volatile substances and mineral impurities.

According to their historical and geological genesis, mineral impurities are traditionally divided into for basic groups.

1. The minerals brought into coal from outside at the early stage of coal formation (quartz, mica, feldspars, pyroxenes, amphiboles, kaolinite, clay minerals);
2. The minerals precipitated from solution at various stages of coal formation (pyrite, marcasite, calcite, dolomite, ankerite, siderite);
3. The minerals originated by precipitation from solutions of surrounding rocks after the coal formation (in the late stages of metamorphism);
4. The minerals brought into during extraction in the form of fragments of enclosing strata.

Normally coal mass includes the following mineral inclusions: large (quartz, pyrite, clay and carbonates), small and trace elements. More than one hundred various minerals and nearly every element in periodic table are found in coal [1-2]. Many elements associated with organic substances or minerals contained in coal are in quantities both significantly exceeding bulk earth values and much less.

Quartz is one of the most widespread minerals, it is present to varying degree in all extracted coals. It is included in other minerals in the form of mixtures and silicates. Pure quartz is colorless or has white color due to internal cracks and crystal defects. Inclusions and microscopic elements of other minerals, mainly oxides of iron, give quartz many and various colouring. It has certain polymorphic modifications which are independent mineral types: cristobalite, tridymite, coesite, stishovite.

The minerals mentioned above have been studied quite well, as evidenced by the published works [3-7].

It is well-known that both coal mining and coal processing have negative impact on the environment: air, water and land pollution. A considerable amount of wastes (slurry) is produced during industrial coal mining and coal processing, which not only pollute the environment but also occupy productive area. Consequently, there arises the task of rational use of coal producing as little waste as possible, as well



as that of search for possible ways to process slurry that is already available. For that purpose it is necessary to conduct a comprehensive study of composition and physical and chemical properties of specific slurry samples produced as a result of coal processing from different coal deposits.

The study of coals and slurry is conducted by different methods of coal petrography, coal chemistry and physics. They include X-ray spectrometry, X-ray diffraction analysis, infrared spectroscopy and ultraviolet spectroscopy, fluorescence analysis, electron microscopy, paramagnetic resonance and nuclear magnetic resonance, thermography, chromatography, oxidation and hydrogenation. Due to the relative simplicity of the method and considerable volume of information obtained, infrared (IR) spectroscopy is one of the most widespread physical methods to study coal and coal products [8-10]. Since theoretical calculations of IR-spectra of molecules and crystalline solids have become possible at the quantum-mechanical level, computational spectroscopy has become an effective additional instrument for interpretation of experimental spectra. It is also the main means of description of their features at the atomic level [11-12].

The purpose of the present work is to determine coal organic mass and mineral part in coal processing slurry and their correlation with the models of the identified slurry components.

2. Research Method

Determination of the content of the major elements of organic mass (carbon (C), hydrogen (H), sulfur (S) and nitrogen (N)) was performed on the Flash EA 2000 elemental analyzer in the mode of dynamic decomposition of the sample in high-purity oxygen gas at a continuous flow of helium at 900-1200 °C. Mineral components in the samples of calcined coal materials were determined by atomic-sorption analysis in plasma discharge of the iCAP 6500 DUO emission spectrometer.

X-ray diffraction pattern of coal materials was registered by the DR-02 "Radian" X-ray diffractometer. When the diffraction pattern was registered, the sample under investigation was scanned according to the following mode: scanning step (0.02°/step) in the angular range varying from 15 to 70° (2 θ) using copper K α radiation (25 kV, 6 mA). Registration of the diffracted radiation was performed using a semiconductor (Si) detector. Crystallographic and crystallochemical database for minerals and their structural analogues "WWW-MINCRYST" were used for analysis of diffraction patterns [13].

To conduct the theoretical part of the research, we used the density functional theory methods (DFT) implemented in the following software packages: Firefly [14] and CRYSTAL [15]. The calculations were carried out using B3LYP [16-17] density functional and TZV basis set [18-19]. Experimental IR-spectra of the samples were obtained on Bruker VERTEX 80 Vc FT-IR Spectrometer in the frequency range from 300 cm⁻¹ to 4000 cm⁻¹.

3. Results and Discussion

Coal slurry of semi-soft coking coal (KS grade coal) was used as an object of the research. The sample was dried at 30°C and ground in a ball mill to obtain a laboratory sample, after that moisture content (W^a -0.39%), ash content (A^a -46.8%) and volatile yield (V^a -11.2%) of the analysis sample were calculated. Elemental composition of coal organic mass, composition and structure of the mineral part and IR spectrum were determined for this sample.

The content of the major elements of organic mass in the sample is shown in Table 1.

Table 1. Content of elements of organic mass in slurry.

Element	N	C	H	S	O
wt. %	1.2	47.0	2.7	0.2	2.9

The total volume of elements constituting organic mass in the slurry is 54 wt. %, which is in good agreement with the calculated independently ash content of the sample (A^a – 46.8%). After recalculation of elements content of coal organic mass by 100%, the following ratio is obtained (N-2.2%; C- 87.0%; H-5.0%; S-0.4%; O-5.4%), which is in good agreement with elements content in semi-soft coking coal

(KS coal grade) [23].

The experimental IR-spectrum of the slurry sample was compared to the spectrum of coal organic mass ($C_{116}N_2H_{88}SO_5$), obtained theoretically within density functional theory (Fig.1).

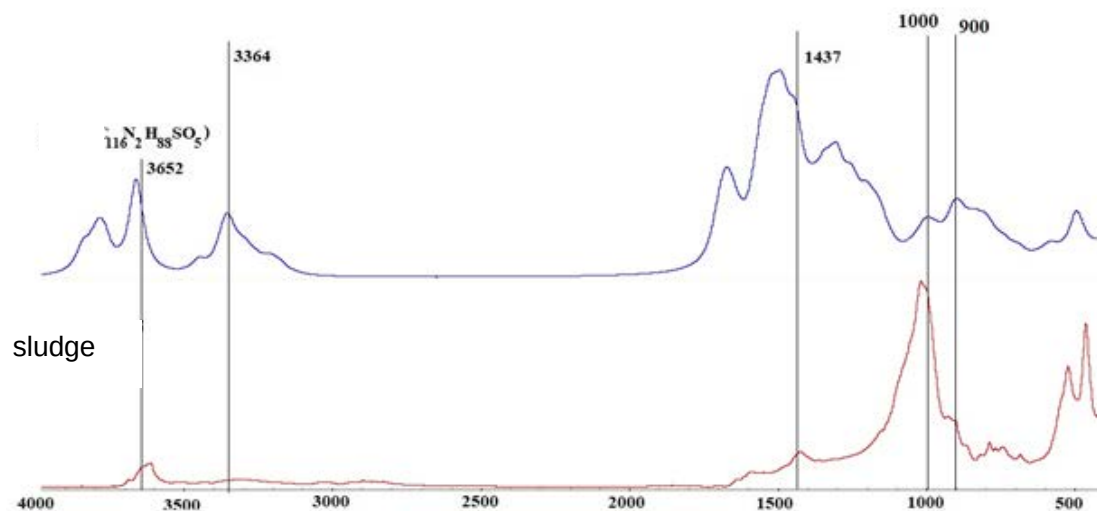


Figure 1. Comparison of IR-spectrum of coal organic mass(COM) with coal slurry spectrum.

The model under consideration is close to semi-soft coking coal in percentage content of chemical elements (KS coal grade) (Table2).

Table 2. Percentage content of chemical elements in organic part of the slurry sample and in 3D-model of COM.

	C, %	N, %	H, %	S, %	O, %
$C_{116}N_2H_{88}SO_5$	85.89	1.73	5.48	1.98	4.93
Organic mass in slurry	87	2.2	5	0.4	5.4
Deviation	1.11	0.47	0.48	1.58	0.47

Analysis of the IR spectrum, obtained theoretically, makes it possible to distinguish characteristic frequency ranges (Table 3).

Table 3.Characteristic frequency ranges for coal molecular model $C_{116}N_2H_{88}SO_5$.

Frequency range, cm^{-1}	Basic vibrational modes
<650	Low-frequency deformation vibrations
650-950	Out-of-plane vibrations of the $C_{ar}H$ group
950-1300	Valence vibrations of the C-O group, deformation vibrations of the $C_{ar}OH$ group, etc.
1300-1700	Deformation vibrations of the CH_2 , CH_3 and $C_{ar}-O$ group; flat vibrations of aromatic ring, $C_{ar}-C_{ar}$ valence vibrations
3000-3500	$C_{ar}-H$ valence vibrations
3500-4000	OH, NH valence vibrations

The comparison of the experimental spectrum of the slurry with the theoretically calculated IR-spectrum of COM reveals coincidence in many peaks. Within 650-950 cm^{-1} frequency range the peak coincidence is observed at 900 cm^{-1} with the shoulder in slurry spectrum; within 950-1300 cm^{-1} frequency range the peak coincidence is at 1000 cm^{-1} ; within 1300-1700 cm^{-1} frequency range the peak in the slurry spectrum is coincident with the shoulder in the IR-spectrum of COM at 1437 cm^{-1} ; within 3500-4000 cm^{-1} frequency range overlapping of peaks is observed at 3652 cm^{-1} . There is a slight deviation of the COM IR-spectrum from the slurry spectrum for some peaks. It should also be noted that the peaks, where both spectra are coincident, are low-intensity peaks in the slurry spectrum. It can be due to the fact that coal organic component in slurry constitute only 54%. Overlapping of peaks with components of inorganic part is also observed. Nevertheless, according to the conducted analysis it can be stated that there is a fairly acceptable correlation between the COM model and coal processing slurry.

The mineral composition of the obtained slurry sample was analyzed at the next stage of the research. The analysis of the diffraction pattern (Fig.2) showed possible presence of silicates in the slurry, such as SiO_2 (quartz), $MgSiO_3$ (magnesium metasilicate) and $CaMg(SiO_3)_2$ (magnesium-calcium metasilicate). Profile analysis of the diffraction pattern was conducted to estimate the quantitative composition of the mineral component of the slurry. (Table 4).

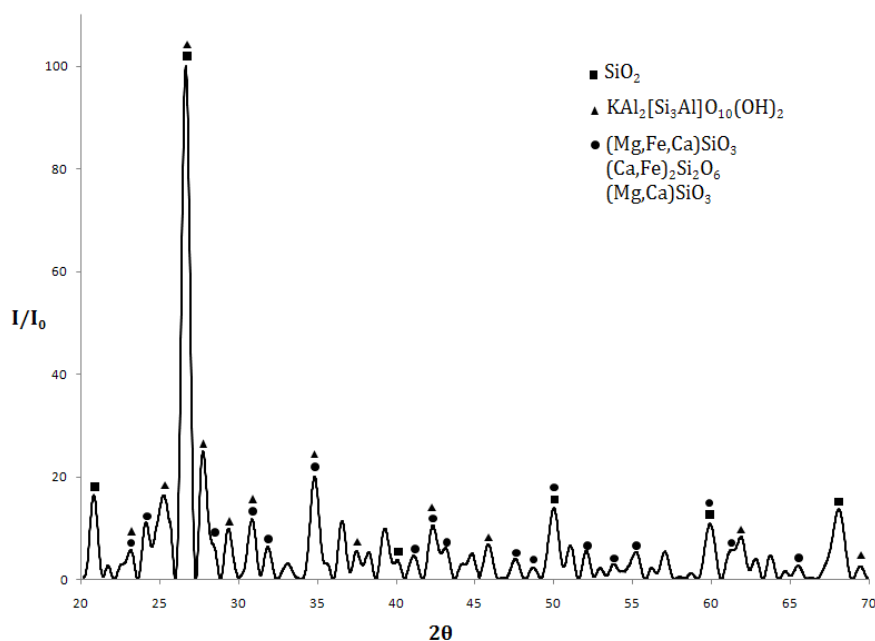
**Figure 2.** Diffraction pattern of semi-soft coking coal slurry.

Table 4. Mineral composition of coal processing wastes (sample 5).

№	Mineral name	Chemical composition	Record № in WWW-MINCRYST database	%, (wt)
1	Quartz	SiO ₂	(7096)	30-40
3	Pyroxenes	Mg(Fe, Ca)SiO ₃ (Ca, Fe) ₂ (SiO ₃) ₂ (Mg,Ca)SiO ₃	(3697) (3700) (1354)	12-20
2	Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	(3021)	35-45
4	Other	-		Up to 23

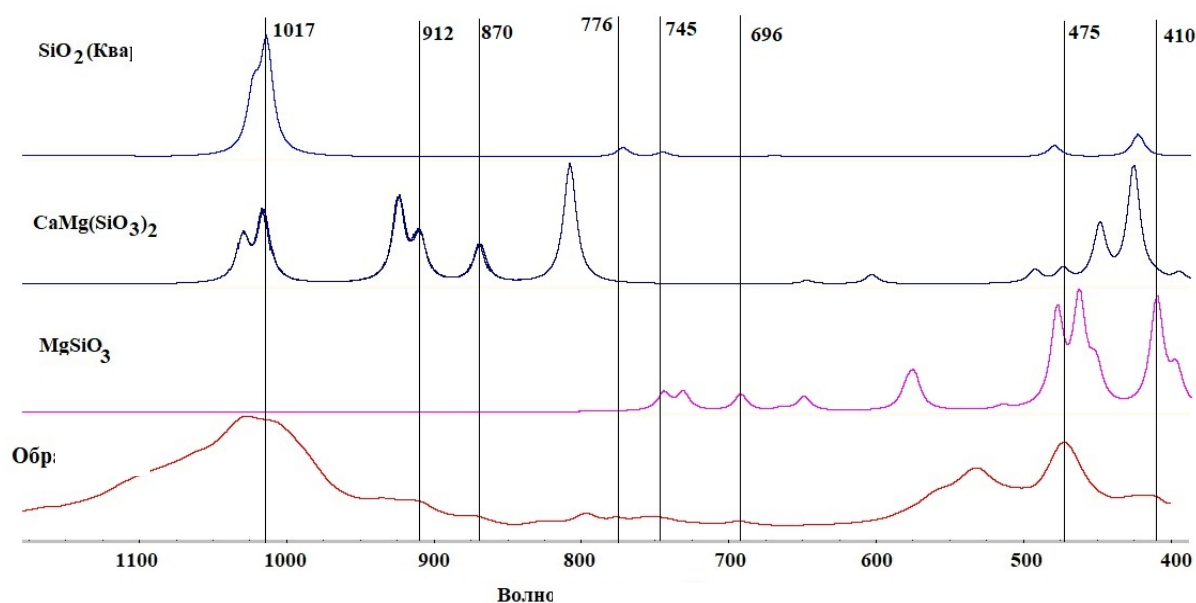
Elemental analysis of the mineral part was determined by atomic-sorption analysis, the results are given in Table 5.

Table 5. Chemical composition of the mineral part of slurry.

[SiO ₂], %	[Al ₂ O ₃], %	[Fe ₂ O ₃]общ, %	[CaO], %	[MgO], %	[MnO], %	[Na ₂ O], %	[K ₂ O], %	[TiO ₂], %
61.6±0.3	16.4±0.1	12.4±0.3	3.9±0.3	1.53±0.01	0.064±0.002	0.19±0.01	3.24±0.001	0.69±0.05

According to the elemental analysis data, a small amount of potassium ions in the mica (muscovite) of the sample is replaced by sodium ions. Due to low concentration it was not possible to detect titanium-bearing minerals. The methods of elemental and X-ray diffraction analysis make it quite possible to determine mineral composition of different types of coal and their slurry.

Theoretical IR-spectra of mineral components of slurry were obtained to conduct further analysis. It is possible to compare the obtained theoretical IR-spectra of the mineral components of slurry with the corresponding (similar) spectra reported in other publications [3-6]. The SiO₂, MgSiO₃ and CaMg(SiO₃)₂ spectra, obtained in our study, have good agreement with the given works [3-6]. There is a slight shift in peaks for quartz.

**Figure 3.** Comparison of IR-spectra of the mineral components with the slurry spectrum.

To confirm the presence of these minerals in the slurry, comparison of spectra of the above-mentioned silicates with the slurry spectrum was performed (Fig.3). The conducted analysis shows coincidence in some peaks for slurry and silicates spectra (Fig.3) (Table 6).

Table №6. Characteristic frequencies in IR spectrum of sample №5 and mineral components.

	ν , cm^{-1}	Vibration type
SiO₂		
Si-O	426, 778	deformation
Si-O	1017	valence
MgSiO₃		
Mg-O	516, 650, 694	deformation, valence
Si-O		
CaMg(SiO₃)₂		
Mg-O, Si-O	426, 473, 650, 1017	deformation
Ca-O	473, 1017	deformation
Si-O	800, 912	deformation

It should be noted that according to the elemental and X-ray diffraction analysis more than 60% of mineral part of slurry comprises silicates, the fact was confirmed by comparison of the IR-spectra where the most intensive peaks are at 426.778 и 1017 cm^{-1} frequencies.

The analysis shows that all the above-mentioned minerals are part of the slurry sample.

4. Conclusions

Using the IR spectra of silicates, as well as coal organic mass, theoretically obtained from first principles calculations, a multicomponent composition of coal processing slurry was studied.

The conducted spectrum analysis allows us to draw conclusion about the composition of the given slurry sample. It comprises both mineral components such as SiO₂, MgSiO₃, CaMg(SiO₃)₂ and organic ones. Given that all the main peaks in the given slurry sample were interpreted, it can be concluded that any other elements, in case they are present in the sample, are in negligible concentration.

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