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Physico-chemical investigation of stone coals of «Karazhyra» field

Results of physico-chemical research of stone coals from the Karazhyra field presents in this work. The following technical indicators of coals were studied: moisture, ash, yield of volatile component, sulfur content, elemental composition, heat capacity, morphology and particle size. The results of the technical analysis indicate low ash and moisture. X-ray fluorescence spectral analysis indicates the presence of rare earth metals in the composition of coal. The surface morphology and particle size of coal samples were characterized by scanning electron microscopy. Results show that the surface is heterogeneous with areas characterized by a dense structure and porous texture. On the surface also observed micron-sized clusters. The average fraction size is 0–300 millimeters. Areas with a porous texture has a corrugated surface with open slit-like and tunnel-like exits forming a system of pores with a size 2–10 microns. Thermal stability was determined by differential scanning calorimetry. On the sample surface was spectroscopically identified oxygen-containing and nitrogen-containing groups. Coal has a relatively high heat of combustion, a high yield of volatile compounds, characterized by a relatively low ash value, moisture, low sulfur and nitrogen content. Demonstrated the possibility of using the Karazhyra field coals in almost all branches of the national economy.

Keywords: stone coals, spectroscopy, X-ray fluorescence analysis, electron microscopy.

Introduction

Stone coals are the largest source of organic raw materials. Its relevance in the near future is significantly increasing due to the depletion of oil, this predetermines the possibility of use it in almost all branches of the national economy from an elementary household furnace to space vehicles [1–4]. Coal is the most complex organomineral formation, and therefore has variety properties. Deep knowledge is need about the features of the chemical structure and reactivity of the organic component of coal and the role of mineral components in the processing and mining of coal. The increased interest in the coals of the Karazhyra field because of their high quality stimulates the search for new innovative methods of its application. Section «Karazhyra» is a coal-mining enterprise of Kazakhstan located in the East Kazakhstan region, on the territory of the former Semipalatinsk nuclear test site. The area of the deposit is 21.4 km², which located 9 kilometers from the site «Balapan» [5]. Coal reserves are 1.3 billion tons [6]. D grade coal produces in this deposit, and the size of the fraction is 0–300 millimeters [7]. The volume of production for 2017 is about 7–9 million tons. According to the journal «Kazakhstan», the coal of the Karazhyra field is suitable for the production of rare earth metals [8]. Previously, the coal extraction process of the Karazhyra deposit was carried out and optimized on the Soxhlet apparatus with organic solvents [9]. According to the results of the extraction products study by IR spectroscopy and chromatography-mass spectrometry (CMS) was shown a preferential presence of alkanes (38.17 %), aromatic hydrocarbons (7.72 %), naphthenes (6.38 %) and oxygen-containing hydrocarbons (5.53 %).

Experimental

Materials and methods

Moisture. Moisture is an important component of coal, from both scientifically and practically point of view. Moisture is ballast and reduces the useful mass of coal when coal is used as energy fuel. Wet coal ignites faster during storage, it freezes at minus temperature throughout transportation, creates certain difficulties on the heat supply route of the combined heat and power (CHP), etc. According to the results of the analysis, the coals of the Karazhyra deposit are generally characterized by a low analytical moisture content, on average, it is 14.0 %. Content of moisture in the fuel depends on several factors: coal mining technology, transportation and storage conditions, natural factors, petrographic composition of coal, coalification degree, formation depth and ash content.

Ash content is one of the most important and the most variable indicators of coal quality. In the course of field operation, additional dilution of coal by rocks of soil, roof or rock interlayers occurs. The average ash content for the deposit was 19.8 %.

The yield of the volatile components of coal from Karazhyra field is average 47.0 % value and depends on the number of microcomponents of the initentite group in the composition of coals. Increasing these components reduces the yield of volatile components.

Coals of the Karazhyra field are low-sulfur, the average content of sulfur is 0.4 %.

Elemental composition of coals is closely related to their physical and technological properties [10]. Determination of sulfur, carbon, hydrogen, nitrogen, oxygen and phosphorus content was carried out on the Labsys Evo analyzer (Setaram, France).

Results and Discussion

The results of the technical analysis of coal presented in Table 1. According to this table the studied coal has low ash and humidity.

Table 1

Qualitative characteristics of coal

No.	Indicators	Index	Average value, %
1	Moisture	W	14.0
2	Ash	A	19.8
3	Yield of the volatile components	V	47.0
4	Sulfur	S	0.4
5	Carbon	C	75.5
6	Hydrogen	H	5.3
7	Nitrogen	N	1.7
8	Oxygen	O	16.8
9	Phosphorus	P	0.04

The *qualitative composition* of the carbon samples was determined from group bands in IR spectra, which obtained by IR Fourier spectrometer Cary 660 FTIR (Agilent technologies, USA). Figure 1 shows the IR spectra of the investigated coal. The spectra show peaks characteristic of stretching vibrations of amides, aromatic hydrocarbons, aromatic and aryl alkyl ethers, alcohol hydroxyls (Table 2).

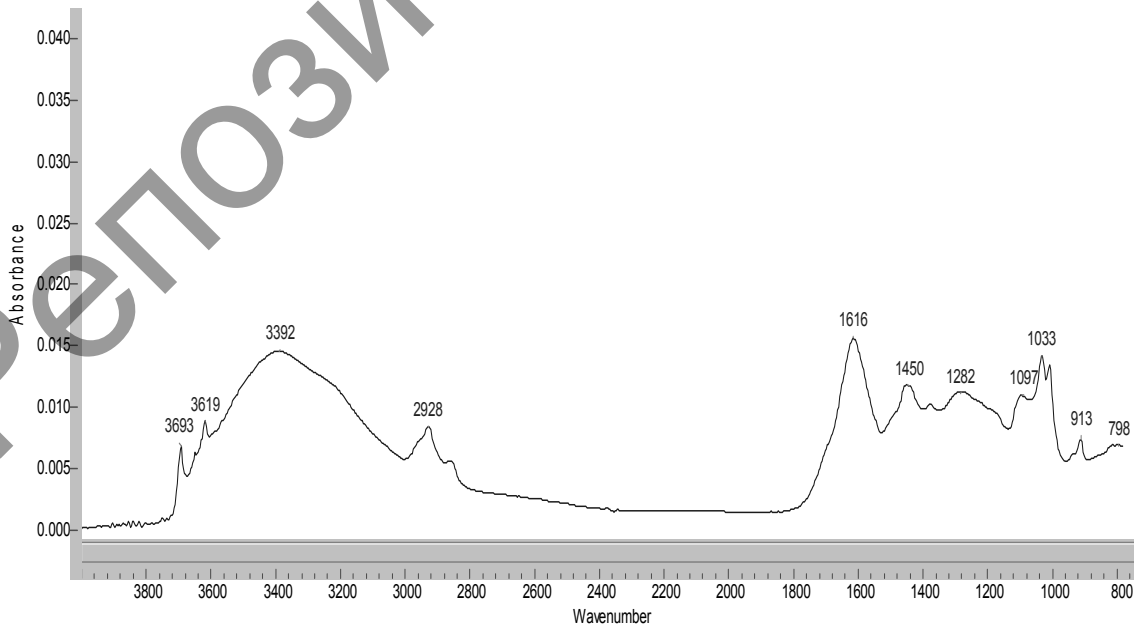


Figure 1. IR spectra of the coal from the «Karazhyra» field

Table 2

Characteristics of IR spectra of the investigated coal from the «Karazhyra» field

Nature of oscillation	Type of groups	Frequency, sm^{-1}
ν_{OH}	Hydroxyl groups	3693 (m), 3619 (m), 3392 (m)
ν_{CH}	Methylene groups in the benzene ring	2928 (m)
$\nu_{C=C}$	Double carbon bonds of primary amides	1616 (s)
ν_{HC-CH}	Unsaturated compounds (aromatic hydrocarbons)	913 (m) – 798 (m)
ν_{COC}	Aromatic and aryl alkyl ethers	1282 (w)
$\nu_{C-O-; -OH-}$	Primary alcohols	1097 (m) – 1033 (m)
ν_{CH2}	Methylene groups	1450 (m)

Note. s — strong; m — medium; w — weak bands.

The investigation of coal samples of the «Karazhyra» field were carried out using an Epsilon X-ray fluorescence spectrometer (Panalytical, Netherlands).

The obtained data are presented in Figure 2 and Table 3. The analysis of XFA showed that the percentage of silicon (5.024 %), aluminum (2.764 %), calcium (2.232 %) exceeds all other indicators. The lowest percentages are zinc (0.008 %), manganese (0.0006 %), chrome (0.011 %). Generally, according to the results revealed 16 elements in the composition of coal.

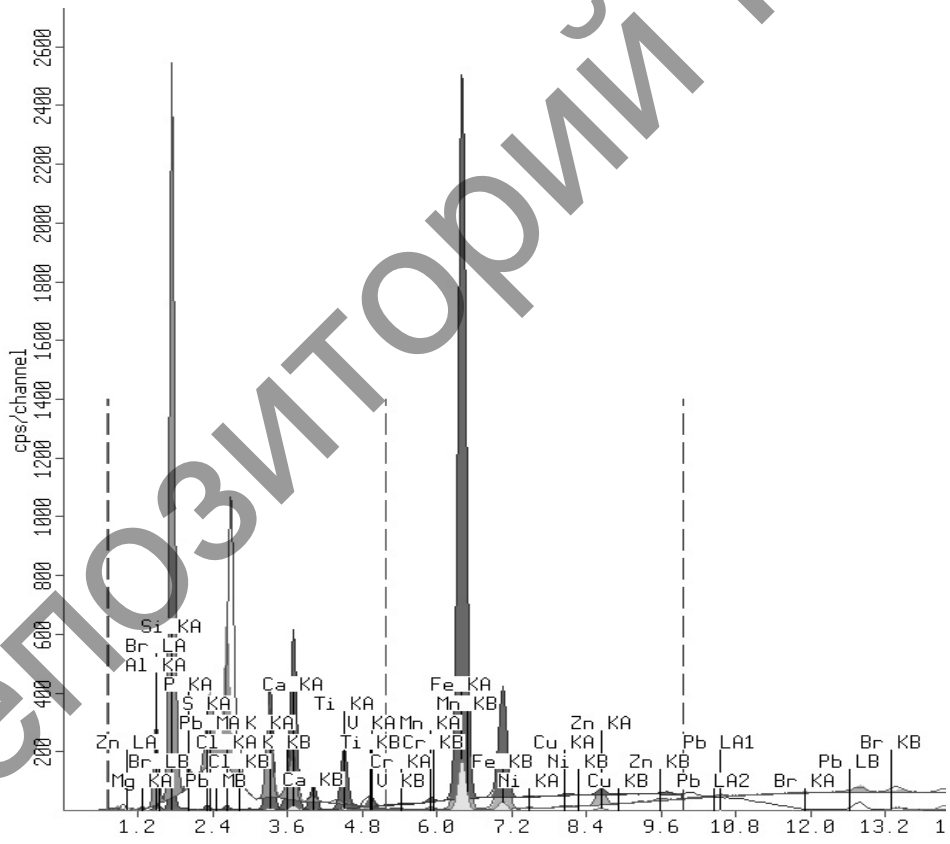


Figure 2. X-ray pattern of the coal sample from the «Karazhyra» field

The morphology and particle size of the coal were determined by scanning electron microscopy (SEM) using a JSM 6390 LM JEOL microscope. Table 4 presents the results of the study. The sample surface is non-uniform with areas characterized by a dense structure and with a porous texture. On the surface also observed clusters with micron size. Areas with a porous texture have a corrugated surface with open slit-like and tunnel-like outcrops forming a pore system with a size of 2–10 μm (Fig. 3, 4).

Table 3

The results of the analysis of the coal sample from the Karazhyra field obtaining by XFA

No.	Element	Sample 1	Sample 2	Sample 3	Average value, %
1	Mg	0.097	0.099	0.095	0.097
2	Al	2.770	2.769	2.755	2.764
3	Si	5.027	5.033	5.012	5.024
4	P	0.432	0.437	0.439	0.436
5	S	1.074	1.070	1.071	1.071
6	Cl	0.445	0.444	0.444	0.444
7	K	0.424	0.426	0.421	0.423
8	Ca	2.235	2.234	2.229	2.232
9	Ti	0.442	0.443	0.441	0.442
10	V	0.021	0.021	0.021	0.021
11	Cr	0.012	0.011	0.011	0.011
12	Mn	0.007	0.006	0.007	0.006
13	Fe	1.469	1.469	1.461	1.466
14	Ni	0.017	0.017	0.017	0.017
15	Cu	0.030	0.030	0.030	0.030
16	Zn	0.008	0.008	0.008	0.008

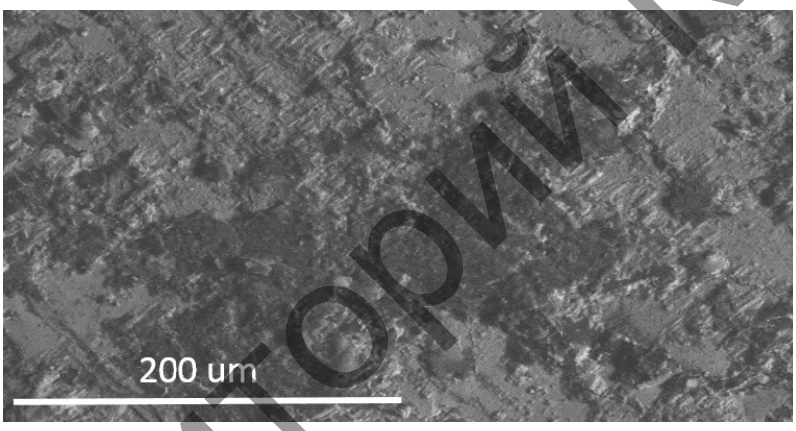


Figure 3. Scanning electron microscope (SEM) image of a sample of coal from the Karazhyra field — a site with a dense morphology of a surface with a porous texture

Based on the data of XFA and SEM, it can be concluded that the results of the analyzes diverge: the use of XFA provides a more accurate and broad list of fixed components in coal composition than SEM. This is due to the fact that XFA allows to explore the entire structure of coal pulverized in powder. A certain section of coal and only the surface are investigated with scanning electron microscopy.

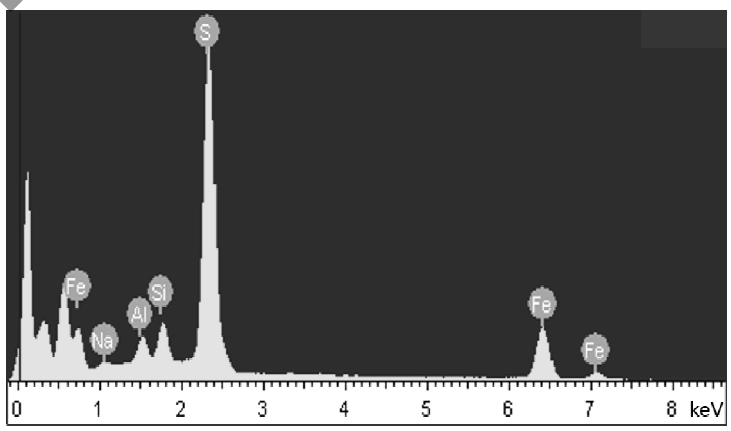


Figure 4. Graph of coal analysis of Karazhyra field by scanning electron microscopy (SEM)

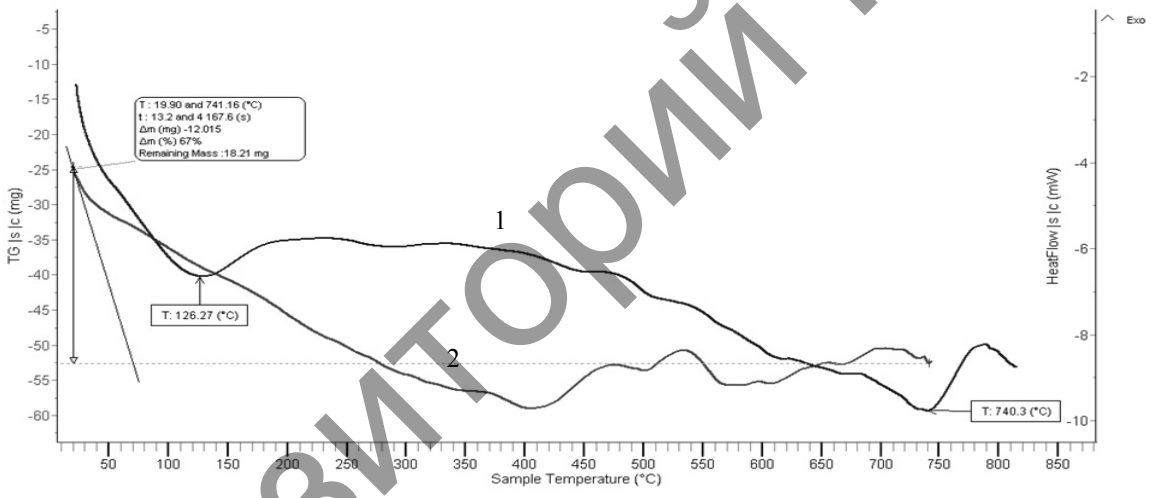
Table 4

Sample analysis result by SEM, %

No.	Na	Al	Si	S	Fe
Sample 1	2.18	3.39	4.94	49.08	40.42
Sample 2	2.19	3.53	5.09	49.36	39.84
Sample 3	2.06	3.59	5.20	48.91	40.24
Average value	2.14	3.50	5.07	49.12	40.16

Thermal stability of the stone coal samples from the «Karazhyra» field was determined on DSC EVO 131 Setaram by differential scanning calorimetry (DSC) (Research were performed on the basis of the «Institute of Polymeric Materials and Technologies» in Almaty). Based on the analysis given in Figure 5, the moisture of the coal evaporates at temperature 126 ºC, and then with further heating of the coal to 750 ºC its structure destroyed. In the range 50–75 ºC the loss of mass of coal was 67 %.

Heat of combustion is the most important characteristic of thermal properties. The higher heat of combustion for dry ashless state Q_s characterizes the natural type of coal, the degree of its coalification and the material composition. The lowest heat of combustion of the working mass of coal Q_i, expresses the amount of heat that can be practically realized during combustion and directly depends on the ash content and humidity of the coal. On average, the lowest calorific value of coal samples is 4650 kcal/kg, at A_a = 19.8 % and W_a = 14.0 %.



1 — coal moisture; *2* — coal ash content

Figure 5. The graph of the interaction of coal from Karazhyra field with heat (with thermal effect)

Conclusion

Thus, the coal of the Karazhyra field belongs to grade D (long-flame), and the fraction size is 0–300 millimeters. Coal has a relatively high heat of combustion, a high yield of volatile compounds, also characterized by a relatively low ash content, and small content of sulfur and nitrogen. Coefficient of grindability of coal is equal to 1.06, so indicates that it is hard coal. With the set of physical methods were identified oxygen and nitrogen containing groups, aromatic compounds, presence of metals. Consequently, the coals of the Karazhyra field are not only good energy fuels, but also an alternative source of raw materials for the chemical industry, and the opportunity to extract it by the open method makes it suitable for use in many areas of the national economy.

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«Қаражыра» кен орны тас көмірін физика-химиялық зерттеу

Мақалада «Қаражыра» кен орны тас көмірінің физика-химиялық зерттеу нәтижелері келтірілген. Көмірдің мына техникалық көрсеткіштері зерттелінді: ылғалдылығы, күлділігі, ұшқыш заттардың шығымы, күкірт мөлшері, элементтік құрамы, жылу сыйымдылығы, бөлшектердің морфологиясы мен өлшемі. Көмірдің техникалық сараптама нәтижелері оның күлділігі мен ылғалдылығы төмен екенін дәлелдеді. Рентгенофлуоресценттік спектрлік талдау көмірдің құрамында сирек кездесетін металдар бар екенін көрсетті. Көмірдің морфологиясы мен өлшемі сканерлеуші электронды микроскопия әдісімен зерттелінді. Көмір үлгісінің беті әртекті, тығыз және кеуекті құрылымды аудандармен сипатталатыны анықталды. «Қаражыра» кен орнының тас көмірі Д (ұзақ жалынды) маркасына жатады. Сондай-ақ беттік ауданда микронды өлшемді кластерлер де байқалды. Фракцияның орташа өлшемі 0–300 миллиметрді құрайды. Кеуекті құрылымды аудандарда, 2–10 мкм өлшемді саңылаулы жүйе түзетін ашық саңылау тәріздес және туннел тәріздес шығуы бар ойықты беттер бар. Термоаналитикалық нәтижелер негізінде тас көмір үлгілері термиялық тұрақты екені, үлгінің бетінде құрамында оттегі және азот бар топтардың болуы спектроскопиялық түрде анықталды. Көмір салыстырмалы түрде жоғары жану жылуына, жоғары шығымды ұшқыш заттарға ие және төмен күлділігімен, ылғалдылығымен, күкірт пен азоттың аз мөлшерде болуымен ерекшеленеді. Aa = 19,8 % және Wa = 14,0 % болғанда, көмір сынамаларының таза каллориялық мәні орташа 4650 ккал/кг құрайды. «Қаражыра» кен орны көмірінің халық шаруашылығының барлық салаларында пайдалану мүмкіндігі көрсетілді.

Кілт сөздер: тас көмір, морфология, спектроскопия, рентгенофлуоресценттік талдау, электронды микроскоп.

Р.Т. Динжуманова, Б.Б. Баяхметова, Н.Б. Касенова, А.Н. Кливенко

Физико-химическое исследование каменных углей месторождения «Каражыра»

В статье приведены результаты физико-химического исследования каменных углей месторождения «Каражыра». Изучены следующие технические показатели углей: влажность, зольность, выход летучих компонентов, содержание серы, элементный состав, теплоемкость, морфология и размер частиц. Результаты технического анализа угля свидетельствуют о его низкой зольности и влажности. Рентгенофлюоресцентный спектральный анализ указывает на наличие редкоземельных металлов в составе угля. Морфологию и размер частиц угля определяли методом сканирующей электронной микроскопии. Установлено, что поверхность образца угля неоднородная с участками, характеризующимися

плотной структурой и пористой текстурой. Уголь месторождения «Каражыра» относится к марке Д (длиннопламенных). На поверхности наблюдаются также кластеры микронного размера. Средний размер фракции составляет 0–300 мм. Участки с пористой текстурой имеют рифленую поверхность с открытыми щелевидными и туннелевидными выходами, образующими систему пор размером 2–10 мкм. На основании термоаналитических результатов установлена термическая устойчивость образцов каменных углей, спектроскопически идентифицированы кислород- и азотсодержащие группы на поверхности образцов. Уголь обладает сравнительно высокой теплотой сгорания, высоким выходом летучих соединений, отличается относительно низкой зольностью, влажностью, небольшим содержанием серы и азота. В среднем низшая теплота сгорания образцов угля составляет 4650 ккал/кг при A_a = 19,8 % и W_a = 14,0 %. Показана возможность применения углей месторождения «Каражыра» практически во всех отраслях народного хозяйства.

Ключевые слова: каменные угли, морфология, спектроскопия, рентгенофлюоресцентный анализ, электронная микроскопия.

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