Molecular spectroscopy analysis of Alagtolgoi coal

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Currently, it is presented the results of a Fourier transform infrared (FTIR) of Alagtogoo (brown coal, abbreviated as At) coal. SEM analysis proved the existence of heavy elements in the coal. Predominantly, they are silicon, aluminum, calcium, iron and oxygen in various compounds. Lesser amounts of the elements iron, magnesium, manganese and sulfur were observed.

Absorptions are spread in the long-wave (2000–400 cm^{-1}) and short-wave (4000–2500 cm^{-1}) zones of the FTIR spectrum. An intensity of the oxygen contained groups in the long wave zone and hydroxyl group band at 3400 cm^{-1} were significant in the coal. Shoulder peaks and the remarkable intensity were noted for the stretching C–H$_{al}$ bands in the short wave zone and bending σ(CH$_3$) bands in the long wave zones.

INTRODUCTION

Coals come to be distributed in various parts of Mongolia however, deposits are concentrated in the north of the country. Paleozoic and Mesozoic coals in the form of anthracite and low volatile bituminous are found in deposits. By the geological forecast it is evaluated that over 152 billion tons of coal reserves, mainly lignite, brown and bituminous coal [1] are present in the country.

Scientifically, the investigation of Mongolian coal was started in Soviet Union times (1950s) and major works have been done on coal geology about exploration and distribution of coal occurrences [2, 3]. Nowadays with the increase of an interest on coal mining, the investigation demand is growing rapidly therefore the works on Mongolian coal structure and chemical processing have been implemented [4-15]. Recently a systematic study on the Mongolian coal geology has been reported by Erdenetsogt B.-O., et al., [16], where the main coal basins in Mongolia were assigned. However, coals from many basins and deposits are not yet in use and their properties were not investigated so far.

Coal is itself highly heterogeneous, macromolecular matrix and its concept of structures still not completely accurate. Molecular structure analysis should be useful for the further useful applications or chemical and physical treatments in the coal. The importance of structural analysis of coal was mentioned in series of previous works [e.g. 1-16] for having detailed information about the understanding of coal matrix structure.

In this work we are reporting experimental results of coal molecular structure studied by Fourier transform infrared (FTIR) spectroscopy to obtain chemical information about the organic solids.

EXPERIMENTAL SECTION

Materials.

Coal sample in this work are from deposits located in the area of Mongolia. In table 1 area and deposit as coal sample was named is given. Coal basin or area was named due to [17].

Table 1. Coal sample.

Basin/Area	Coal deposit	Label
Eastern Mongolian province(Eastern Mongolia)	Alagtogoo	At

Alagtogoo (in some sources it has named as Alagtolgoi, but here we named due to [17]) coal deposit is located in Dornogobi aimag, Central Mongolia, 330 km from southeast Ulaanbaatar and has estimated bituminous coal reserve of 872 Mt. Deposit is an open-pit and a mining produces 5 Mt annum.

Sample preparation for analysis was performed in accordance with standard procedures of coal chemistry: A piece of coal from each deposit was crushed initially and then mill to a size of 0.05 mm or less by using agate mortar in an argon flow glove box. At last, milled samples were kept in Schlenk flask under argon.

Methods.

Scanning electron microscopy (SEM/EDS): Coal samples were analyzed by scanning electron microscope (JOEL) equipped with backscattered and secondary electron detectors coupled with energy dispersive X-ray spectrometry (EDS). The SEM–EDS provides detailed imaging information

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about the morphology and surface texture of individual particles, as well as elemental composition of sample.

In this study, backscattered electron imaging (BSE) which provides visual information based on gray-scale intensity between chemical phases and EDS were used to characterize heavy elements in coal samples. At the same time, secondary electron imaging (SEI) images of the coal samples also have been done with magnification up to 10^4.

The elemental composition of coal samples is determined using characteristic X-ray spectrum up to 20 kV on the surface of the coals. The elemental analysis was performed in a ''spot mode'' in which the beam is localized on a single area manually chosen within the field of view. The location is represented on the provided SEM images by a ''+''. The EDS detector was capable of detecting elements with atomic number equal to or greater than six.

Fourier Transform Infrared (FTIR) spectroscopy: Functional groups of the samples were detected by the In situ Fourier Transform Infrared (FTIR) Nicolet Avatar 330 Spectrometer, in transmittance mode. Raw coal samples were firstly dried in an oven at 110^0C for 72 hrs and prepared by grinding with KBr (optimized mass ratio of coal to KBr was 1:50) using a mortar. Thus, every pellet scanned from 250 times ranged from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM): In figure 1 it is shown At coal SEM images about size determination where coal surface is bombed by rays with 10 keV and a morphology with 20 keV, magnified up to 10000 times. The sizes of the coal particles ranged from less than 5 µm to greater than 200 µm. However, particles ranged in size from approximately 5 to 100 µm are main consistent. Carbon content majority surface was dark vision, although brighter spots on the surface had high contents of heavy elements, which are listed in table 2. Similar results are taken for other coals as well.

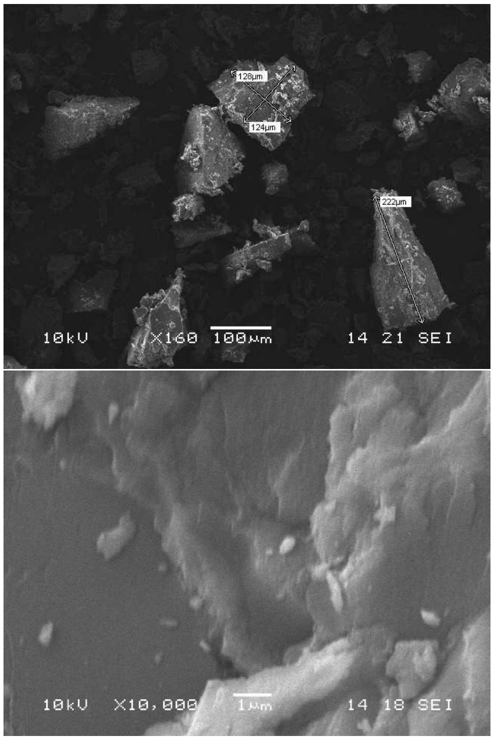

Figure 1. SEI images of the At coals: 10 keV rays, magnification 160 times and size determination (left), 20 keV rays with a magnification of 10000 times (right).

As determined by EDS, the predominant elements in the coals were silicon, aluminum, calcium, iron and oxygen in various compounds (Table 2). Lesser amounts of the elements iron, magnesium, manganese and sulfur were observed. Aluminum was primarily associated with silicon.

Barium and silver are found in At coal on their bright spots.

Table 2. Heavy element contents in the At coal in according to EDS.

Coal sample	Element content, wt.%											
	C	O	Al	Si	Ca	S	Fe	Se	Mn	Mg	Ag	Ba
At	73.62	15.99	0.83	2.38	1.66	1.08	0.66	2.48	0.37	0.03	0.09	0.77

FTIR spectroscopy: Analytical data on the coal is provided by FTIR spectroscopy result. In table 3 the peaks are precisely given for the studied coal sample.

Peaks are spread in the long-wave (2000–400 cm^{-1}) and short-wave (4000–2500 cm^{-1}) zones of the FTIR spectrum.

A broad intensive band around 3400 cm^{-1} due to O-H and N-H stretching of various intermolecular hydrogen bonded groups like phenols and alcohol. Also, water present in the small pores of the mineral particles gives rise to a band at 3280 cm^{-1} [18], which is registered in At coal spectrum.

In the area of stretching of CH$_x$ group (2800–3100 cm^{-1}) there are observed three intense absorption bands with maximums at 2951, 2920 and 2850 cm^{-1} for the sample. Bands at 2920 and 2850 are from stretching (symmetrical and asymmetrical) vibrations of aliphatic group CH$_2$ and CH$_3$ relatively. However, concentration of hydrocarbon is proportionate with integral intensity of stretching band of CH$_x$-group [19], thus can be approved that in the studied coal it is existed predominantly in state of CH$_2$.

Further goes a broad band in the area of 1700-900 cm^{-1} that wholly gives important information about coal structure and content. In consequence of a strong overlapping in this area, interpretations are always ambiguous.

The broad band in the area 1600 cm^{-1} for the studied coal provides a carbonyl group in aromatic ring characterized by sp^2-carbon or carbonyl absorption from conjugated hydrogen bonded carbonyl groups, or due to donor and acceptor interaction between aromatic carbon macromolecules. A poorly defined band around 1700-1650 cm^{-1} on its shoulder is assigned to a vibration of carboxyl groups C=O (aldegydes, ketones and unsaturated aryl aldegydes) [20].

The bands around 1400 and 1300 cm^{-1} are assigned to the bending of CH$_2$ and CH$_3$ groups [21, 22]. Three bands near 1490, 1440 and 1385 cm^{-1} are available whose intensity correlates preferentially with the intensity of bands from carbonate minerals in the area 1300-900 cm^{-1}. Despite the bands near 1400 are contributes to the presence of minerals [18], the identification of minerals such as clay minerals in the current area remains very difficult because of their complicated and non-constant composition and also because band positions can vary highly owing to isomorphous replacements.

Furthermore, the mineral fraction of coal is usually a poly-component system and as a result, provided that one mineral is not predominant, the complexities of the overlapping may preclude a straightforward interpretation. Thus, in according to the literature [23, 24] the various spectral bands at 1040, 870, 800, 750 cm^{-1} and lower are compatible with vibration of minerals in different types.

By spectrum intensity, the peaks lower than 1100 cm^{-1} considerably distinguish. The peak at 1040 cm^{-1} is the most intensive in the whole spectrum. The peak at 914 cm^{-1} is assigned to the out-of-plane vibration of hydroxyl. A presence of the bands of 1160 and 1040 cm^{-1} calls the band near 694 cm^{-1} is resulting from quartz [18]. Aromatic ethers band around 1260 cm^{-1} is highly overlapped and poorly defined for the studied coal.

Table 3. FTIR peaks in the infrared spectra of the coals and their assignments. Valence vibration symbolized by υ, deformation vibration by — σ, vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder

Assignment	**Peak, cm^{-1} / As received coal**
stretching ν(O–H)	3415m 3280m
stretching ν(C–H$_{al}$)	2958w 2920w 2868w 2850w
bending ν(C$_{ar}$–O)	1695sh,m 1612vs
bending σ(CH$_2$) **bending σ(CH$_3$)**	1480s 1440vs 1383vs
stretching σ(C-O-R) **stretching σ(C-O)**	1280s 1217s 1165s
Stretching υ(Si-O-Si)	1041m
out-of-plane bending σ(C-H)	870w 810w 750vw
bending or stretch σ(Si-O), σ(Si-O-), σ(Si-O-Al), or σ(Al-OH)	530vw 470vw

The prominent bands in the short-wave zone are three bands at 870, 800 and 750 cm^{-1} from isolated out-of-plane deformational vibration (890-850 cm^{-1}) or two-adjacent (830-815 cm^{-1}) or three-adjacent (800-775 cm^{-1}) of *sp*^{2}- hybrid bonded aromatic CH-groups. The band at 750 cm^{-1} is overlapped with the band at 800 cm^{-1} essentially. These bands at 800 cm^{-1} and 750 cm^{-1} are an evident of different kinds of quartz in the coals [23]. Peaks in the low frequency 530 and 470 cm^{-1} in the spectrum are quite intense comparing to those of other coals. The probable assignments to these bands are e.g. Si-O bending or stretch, Si-O-Al deformation, Al-OH stretches and OH translations [25] by agree with element content.

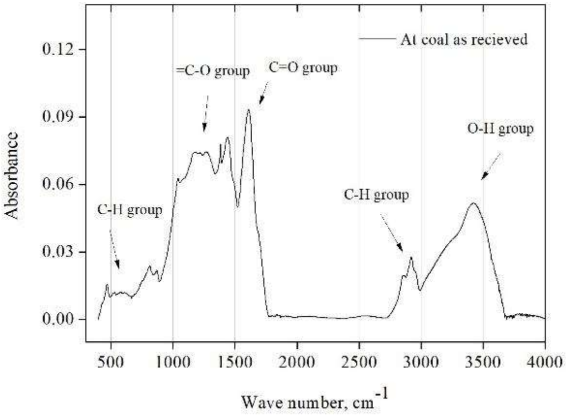

Figure 2. FTIR spectrum of At coal as received

CONCLUSION

A study about the molecular analysis of the brown type Mongolian Alagtolgoi coal is presented on the basis of spectroscopic study.

SEM analysis proved the existence of heavy elements in the coal. Predominantly, they are silicon, aluminum, calcium, iron and oxygen in various compounds. Lesser amounts of the elements iron, magnesium, manganese and sulfur were observed.

Absorptions are spread in the long-wave (2000–400 cm^{-1}) and short-wave (4000–2500 cm^{-1}) zones of the FTIR spectrum. An intensity of the oxygen contained groups in the long wave zone and hydroxyl group band at 3400 cm^{-1} were significant in the coal. Shoulder peaks and the remarkable intensity were noted for the stretching $C–H_{al}$ bands in the short wave zone and bending $\sigma(CH_3)$ bands in the long wave zones.

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