

these coals from first environment to second have no significant change and it is broad up to 7 Gs.

The saturation curve shows the one of components saturation character or broad (in the presence of air mostly) or narrow (in the flow of nitrogen gas mostly). The EPR spectra with two components in the coal has discussed in many of works [2, 3] that mainly attributed to two types of macerals (fusain and vitrain, respectively) in the coal. This is also proved by the dependences of atomic hydrogen-carbon ratio of the studied coals that particularly the lower group coals show the complexity in their EPR spectra. The narrow component is alleged to the presence of fusain (or inertinite) that is composed mainly of fusinite or carbonized woody plant tissue. One can also assign it to the coal spontaneous combustion since the same EPR property has observed on particular samples taken from the place where the coal self-inflammation center is. Broad component is attributed to the existence of vitrain in coal, which composed primarily of the maceral group vitrinite. Therefore, the observed absorption spectra in our case which regarded as two-components, the broad and narrow lines are attributed to the paramagnetic centres of vitrinite and inertinite, respectively. It is clear from the measurement results that the broad line is much more easily saturated, exposing a relatively weaker narrow line at high microwave power. The appearance of the narrow line is coal rank independent.

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ADVANCED PULSE EPR STUDY OF NATURAL MONGOLIAN COALS

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CONTINUOUS WAVE ELECTRON PARAMAGNETIC RESONANCE (CW EPR) METHOD

The continuous wave EPR spectra were obtained in the solid state at room temperature (300 K) in glass tubes in a presence of air (I) and in a flow of nitrogen gas (II). The samples were in size of greater than 5 mm and weighted nearly 30 mg. Sample mass is meas-

ured on the Mettler Toledo AE 260 micro balance and size on SMZ-140 series Stereomicroscope with magnification range $\times 40$.

A Bruker Elexsys II E500 X-Band spectrometer was used operating at a frequency of 9.8 GHz, with a 100 KHz modulation frequency, 0.01-0.1 mT modulation amplitude and ≤ 200 mW microwave power (200 mW at 0 dB attenuation).

The spectrometer was equipped with a super high Q-factor resonator (ER 4122 SHQE) which has a cylindrical shape TE_{011} cavity.

Modulation amplitude and time constant of EPR registration were chosen from well-known requirements for undistorted registration of the first derivative resonance absorption signal by magnetic induction.

EPR spectra of the studied coals were registered as the first derivative of the microwave absorption versus applied magnetic field. The parameters of the EPR spectra: g-factor, linewidth (ΔH_{pp}) and integral intensity (I_{pp}) were evaluated. g-factor was determined as $g = h\nu/\beta H_r$, where h is the Planck constant, β the Bohr magneton, ν the microwave frequency, and H_r is the resonance magnetic induction. The linewidth (ΔH_{pp}) was determined as the difference of field positions of maximum and minimum of the first derivative EPR spectrum. The integral intensity (I_{pp}) is the distance between maximum and minimum of the first derivative EPR spectrum (figure 1).

Coal free radicals or the integral intensities of the EPR signals were detected and quantified using the approximation: $(\text{the derivative amplitude} \cdot \Delta H_{pp}^2)/\text{sample mass}$.

Simulation of CW EPR spectra was done using the Matlab package EasySpin [21].

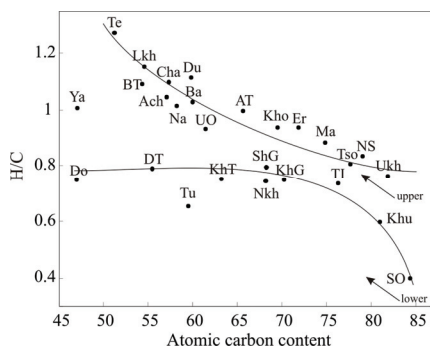


Fig. 1 Hydrogen atom contents (H/C in atomic unit) vs. carbon contents (in atomic unit)

Firstly, the coals went under the determination of the elements C, H, N, O and S which has been carried out with instruments of the company LECO at the Micro Laboratory for Organic Chemistry (ETH, Zurich). The samples were digested first and the combustion products - carbon (CO_2), hydrogen (H_2O), sulfur (SO_2) and oxygen (CO_2) are analyzed quantitatively by infrared spectroscopy. Nitrogen (N_2) is determined by a thermal conductivity detector. These variables are measured in weight percent (wt. %) and are calculated in the air-dried (ad) base. Dependence between carbon content in studied coals and their atomic ratio of H/C is shown in figure 1. Due to this dependence

the coals are grouped into upper and lower as following:

Upper group: Baganuur (Ba), Tevsh (Te), Aduunchuluun (Ad), Bayanteeg (BT), Yavar (Ya), Logiin-Khar (Lkh), Duvunt (Du), Chandgana (Cha), Maanit (Ma), Alagtogoo (AT), Ereen (Er), Ulaan-Ovoo (UO), Ukhoo-Khudag (Ukh), Tsagaan-Ovoo (Tso), Nariin-Sukhait (NS), Khotgor (Kho).

Lower group: Dov Tal (DT), Dovt (Do), Tugrug (Tu), Khar-Tarvagatai (KhT), Shariin-Gol (ShG), Tavantolgoi Seam I and IV (TI and TIV), Nuurtskhotgor (Nkh), Khushuut (Khu), Khuren-Gol (KhG), Saikhan-Ovoo (SO).

Approximately 30 mg of each coal was carefully transferred to the quartz sample tubes. Firstly, the continuous wave EPR spectra were obtained at Bruker Elexsys II E500 X-Band

spectrometer operated at a frequency of 9.8 GHz at room temperature. The advanced measurements were carried out with an X-band pulsed EPR spectrometer Bruker Eleksys E-580 under a flow of nitrogen gas (ETH Zurich). A dielectric resonator with a low Q-factor of about 300 and a 1.2 kW TWT amplifier were employed.

The microwave (mw) pulse sequences for the EPR spectroscopy used in this work are shown in figure 2.

A two-pulse echo experiment ($\pi/2-\tau-\pi-\tau$ echo) was used to measure field swept echo signal in X-band. T_2 measurements have been directly made with spin echoes. For the determination of the longitudinal relaxation time, T_1 , the three-pulse inversion saturation recovery experiment ($\pi-\tau-\pi/2-\tau-\pi-\tau$ echo) was used.

The hyperfine sublevel correlation (HYSCORE) spectra were recorded employing the sequence $\pi/2-\tau-\pi/2-t_1-\pi-t_2-\pi/2-\tau$ -echo with mw pulses of length 16 ns and 24 ns for the $t_{\pi/2}=90$ and $t_{\pi}=180^\circ$ pulses, respectively. The time interval τ between first and second microwave pulses was fixed 112 ns. Unwanted echoes were removed by means of a four-step phase cycle.

The echo decay was eliminated by a second-order polynomial baseline correction in both time domains, applying a Hamming window and zero-filled to 1024 data points in both dimensions. After 2D Fourier transformation absolute value spectra were calculated.

For all coals have been measured the field swept electron spin-echo (ESE) spectra. A spin echo has not been observed for the Ba coal. In figure 3 the field swept ESE spectra in two-pulse experiment for several samples are shown. The symmetric field swept ESE spectrum was recorded for the upper group coals Te, Ad, BT, Ya, Lkh, Cha, Ma, KhT. These coals (except KhT) are vitrinite rich lignites and subbituminous coals. For the same upper group coals as AT, Er, UO, Ukh, Tso, NS, Kho and lower group coals as ShG, DT, Do,

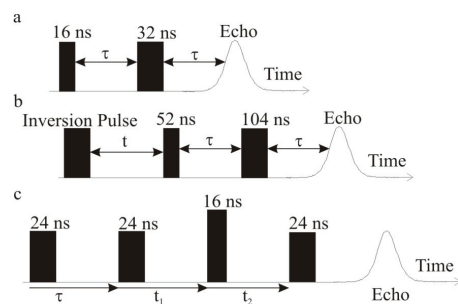


Fig. 2. Pulsed EPR experiments employing a variety of multiple pulse schemes a – a two-pulse echo, b – the three-pulse inversion saturation recovery experiment, c – HYSCORE

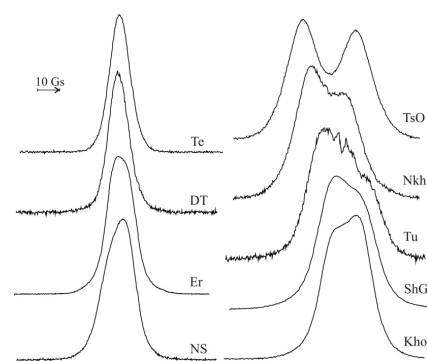


Fig. 3. Field swept ESE, two-pulse field swept echo detected spectra. The time, τ , between the 90 and 180° pulses in the two pulse echo sequence was 400 ns.

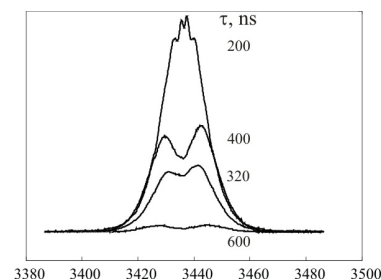


Fig. 4. Amplitude change of the coal due to the pulse interval (τ)

Tu, TI, TIV, Nkh, Khu, KhG, SO, the ESE spectra were asymmetrical or the spectra with dip at the central part.

When the pulse interval (τ) was increased from 200 to 600 ns the amplitude of the coal was changed dramatically (figure 4). Moreover, the dip depth depends strongly on the value of τ and pulse length (figure 5).

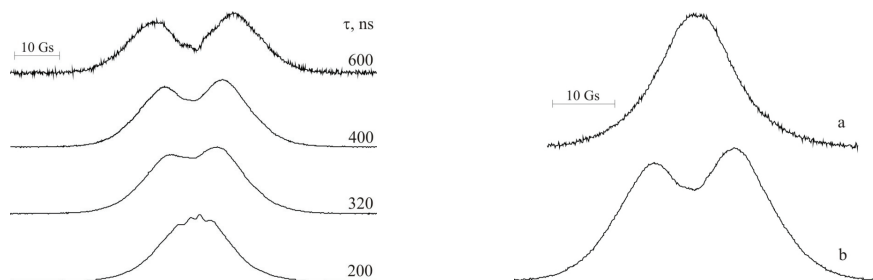


Fig. 5. Magnetic field swept ESE, two-pulse field swept echo detected spectra of TI coal obtained at several values of τ and at different pulse lengths (a – 16 and 32 ns, b – 24 and 48 ns)

A peak-to-peak width of the cw EPR spectra was in the interval 0.5-0.7 mT (14-20 MHz) for the coals such as SO, UO and NS, At, ShG, Er (except DT, Kho, Do) whose dip at the field swept spectra in the same condition (at the same pulse length and interval) is smaller than that of 0.1-0.3 mT (2-8 MHz) linewidth coals such as Tso, Tu, TI and TIV, UKh, Khu, KhG and Nkh. This shows the sensitivity of the appearance of the dip and asymmetry of the field swept spectra to the spin-spin relaxation time which accords to many early works [1, 2]. Due to [2] the appearance of dip can be originated from three main reasons: a fast spin relaxation process, or a decrease in the number of interacting nuclei, or the certain fast relaxation process such as “instantaneous diffusion”. As mentioned above lower group coals and high rank coals from upper group are declined to the asymmetry and the appearance of dip in the field swept. Consequently, the phenomenon could be assigned to the coal different maceral types that have different spin-spin relaxation times.

The relaxation times for the coals have been measured in a few cases. It is well known that relaxation times determine both saturation and linewidth. Coal spin-lattice time, T_1 , relates with the coal spin concentration and molecular motion and the coal spin-spin relaxation time, T_2 , relates to the linewidth.

The results of T_1 and T_2 relaxation times of some coals are shown as dependences of linewidth (Figure 6) and the elements contents (Figure 7). A trend is that T_1 values are in range of 30 ± 10 μ sec in most coals. The plots of T_1 against the atomic hydrogen and oxygen to atomic carbon ratios show the decrease in the T_1 values with an increase of the elements. Among those lignites, KhT coal has the highest spin concentration that might cause the greatest value of T_1 . T_1 is monotonously decreasing in the increase of linewidth.

Generally, spin lattice relaxation in the whole coals have individual differences in dipolar anisotropies or molecular motion dependent of the coal rank and the heteroatom contents such as carbon, hydrogen or oxygen in the established experimental regime.

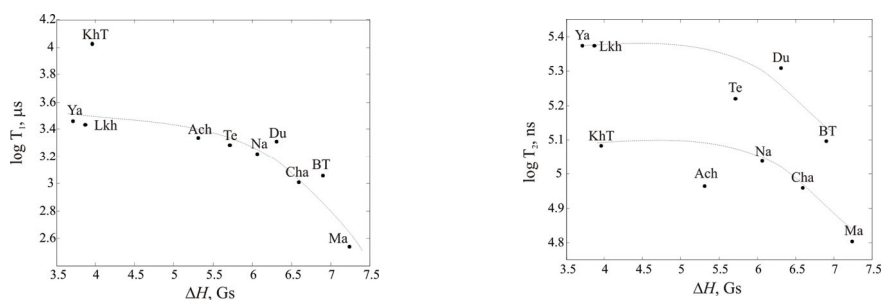


Fig. 6. Spin-lattice relaxation time, T_1 (s) and spin-spin relaxation time, T_2 (s), versus linewidth (Gs)

In the range of T_2 , lignites are distributed in two levels. In the upper level are for the coals Ya, Lkh, Te and Du and lower for Ma, BT, Na, Cha, Ad and KhT. If the only relevant EPR-parameter is the peak-to-peak amplitude of the first derivative signal, taken as a measure of the number of radicals in the sample, thus the distribution of coals proves the strongly correlation between T_2 and coal spin concentration, since upper level coals have the smaller intensity than lower coals. As H/C and O/C increase, T_2 is tendentious to decrease (figure 7) for both level coals. The same dependence in linewidth on T_2 was observed (figure 6).

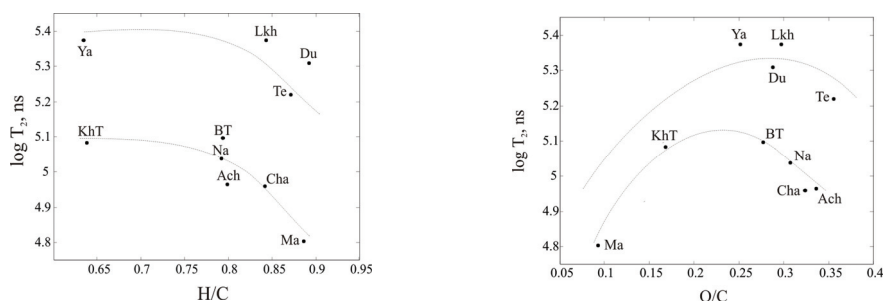


Fig. 7. Spin-spin relaxation time, T_2 (s), versus atomic ratio H/C and O/C

For the characterization of the paramagnetic species in coal, we have also applied hyperfine sublevel correlation spectroscopy (HYSCORE) method. This method enhances the frequency resolution of the spectrum that makes possible to observe hyperfine structure under the symmetrical, singlet, broad EPR signals. The hyperfine signals due to ^1H (around 14.8 MHz) and naturally abundant ^{13}C (around 3.7 MHz) are clearly appeared in the spectrum of lignite coal KhT. For the high rank coals as TI and SO a signal was registered only from the ^{13}C .

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