RELATION BETWEEN THE PETROGRAPHIC AND CHEMICAL PROPERTIES OF WEAKLY REDUCED AND REDUCED COALS OF DONETS BASIN

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A b s t r a c t . Low-rank coals of the same rank level but of different genetic types and different tendency to self-ignition have been studied by means of coal chemistry. It has been shown that oxygen- and sulphur-containing functional groups, especially bridge-bonds, are responsible for the structure and properties of pyrolysis products.

K e y   w o r d s : coal, vitrinite, petrography, Donets Basin.

INTRODUCTION

It is well known that the predominant depositional environment determines development of coal facies. Coals deposited in brackish — marine areas are distinguished by the high content of hydrogen, nitrogen, sulphur, and especially by the presence of finely crystalline pyrite concretions. Marine-influenced bituminous coals have special properties (Geological-geochemical map..., 1954; Teichmüller, Forzschr, 1974; Matsenko, Saranchuk, 1980; Matsenko, 1984; Volkova, Bogdanova, 1989).

Structure and reactivity of these coals have not been studied deeply enough though the high sulphur content is a serious problem for their utilisation.

The aims of this paper are a detailed study of different genetic coal types (reduced and weekly reduced) using the chemical, physico-chemical, and petrographic techniques, and explanation of the interconnection between coal structure and its tendency to self-ignition and thermal transformation.

EXPERIMENTAL

The samples of reduced and weakly reduced coals were collected from the coal seams of Donets Basin in closely spaced locations (the distance between stratigraphic columns was less than 100 m). Donets Basin is a classical example of Carboniferous coal accumulation in which coal-bearing deposits are polyfacial, i.e. alluvial and marine. Therefore, one of the most important genetic characteristics of these coals is reductivity of the vitrinite, depended on the facial parentage. Three pairs of coals of the same rank level (low-rank), but of different genetic types and different tendency to self-ignition, were selected for this paper.

The petrographic, proximate and ultimate analysis of the samples, including the total (S_t), organic (S_o), pyritic (S_p), and sulphates (S_s) sulphur were determined by standard procedures.

Pyrolysis in steam flow was made by Minkova *et al*. methods (Bulgarian Academy of Sciences).

Differential thermal analysis of the samples was carried out in a Paulic-Paulic-Erdei Q-1500D thermobalance at the heating rate of 10^oC min^{-1} in a closed platinum crucible.

IR — spectra of solid fuels were recorded on a FT-IR "Bio-Rad" FTS 7 spectrometer using the DRIFT technique.

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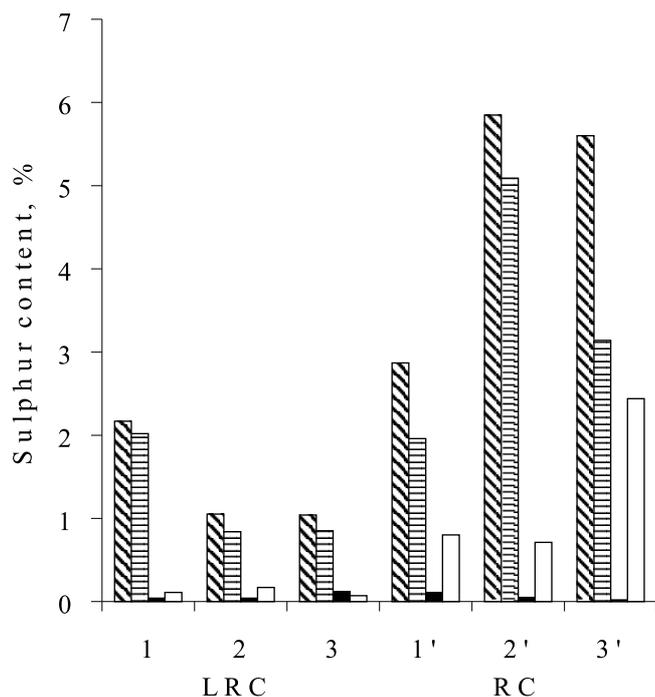[3] Donetsk State Technical University, 48 Artema str., Donetsk 83000, Ukraine
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RESULTS AND DISCUSSION

Characteristics of the coals are summarised in Table 1 and 2. As can be seen from Table 1, samples of reduced coals (RC) are distinguished by higher total sulphur content and H/C ratio, yields of volatile matter higher than it would be expected from their degree of coalification, and as compared with weakly reduced pairs.

Petrographic composition of coals is uniform enough, with predominant presence of vitrinite (Table 2). The lower value of vitrinite reflectance (R_m^o) and higher content of lithotypes with finely crystalline pyrite are recorded in RC samples.

Total sulphur was subdivided as follows: $S_t = S_s + S_p + S_o$.

There are differences in all the sulphur functions between RC and LRC coal types (Fig. 1). Higher S_o^d and S_p^d sulphur contents were determined in reduced coals in all pairs.

For coals under study, an organic sulphur S_o is the main form of sulphur. Moreover, a linear relationship between S_o^{daf} and V^{daf} is obvious (Fig. 2).

The influence of coal genetic types on their behaviour in the pyrolysis was also taken into account. Results from proximate and ultimate analyses for pairs of initial coals and their semi-cokes are gathered in Table 3. It can be seen from the table that solid products of steam pyrolysis were characterised by high ash, carbon contents and well developed surfaces.

Fig. 1. Distribution between different types of sulphur in initial coals
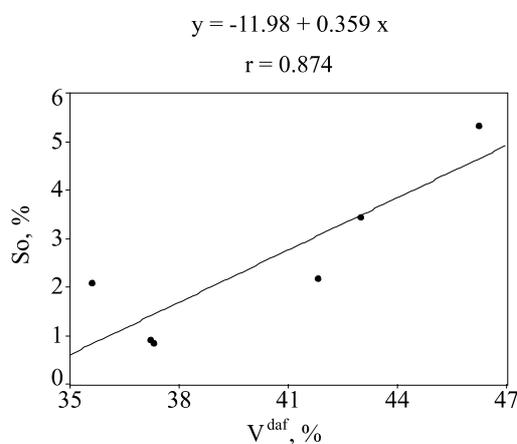
Fig 2. Correlation among the organic sulphur content and yields of volatile matter

$$y = -11.98 + 0.359\, x$$
$$r = 0.874$$
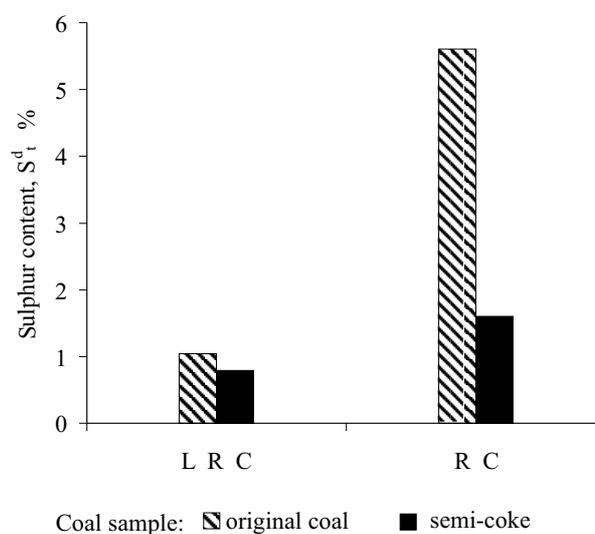
Fig. 3. The change of sulphur content in different coal types after thermal treatment
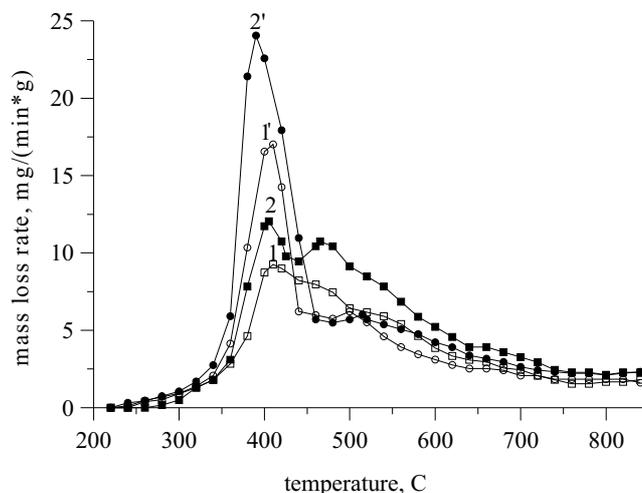

Fig. 4. Temperature dependence of mass loss rates for LRC and RC pairs with different tendency to self-ignition

Table 1

Characteristics of initial coals, [wt %]

Number	Coal mine, seam	Type	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	N^{daf}
1	Cheluskintsev, l_4	LRC	0.8	2.4	35.6	79.3	4.94	2.32
2	Trudovskaya, l_4	LRC*	1.0	1.6	37.3	78.4	4.95	1.90
3	Kurakhovskaya, l_4	LRC	9.4	5.3	37.2	79.3	5.07	—
1^1	Ukraine, k_8	RC	1.5	9.9	41.8	77.9	5.30	2.10
2^1	Trudovskaya, k_8	RC*	0.9	4.6	46.2	76.1	5.43	1.97
3^1	Kurakhovskaya, l_2'	RC	5.5	8.6	43.0	76.1	5.22	—

Number	Coal mine, seam	(O+S+N)diff	S_t^d	S_s^d	S_p^d	S_o^{daf}	H/C, [atm]
1	Cheluskintsev, l_4	15.76	2.17	0.11	2.02	2.07	0.75
2	Trudovskaya, l_4	16.65	1.05	0.17	0.84	0.85	0.76
3	Kurakhovskaya, l_4	15.63	1.04	0.07	0.85	0.90	0.77
1^1	Ukraine, k_8	16.80	2.87	0.80	1.96	2.17	0.82
2^1	Trudovskaya, k_8	18.47	5.85	0.71	5.09	5.33	0.86
3^1	Kurakhovskaya, l_2'	18.68	5.60	2.44	3.14	3.43	0.82

Table 2

Vitrinite reflectance and petrographic composition of low-rank coals of different genetic types

Number	Coal mine, seam	Type	$\overline{R}_m^o$, [%]	Organic components, [%]			Mineral components, [vol.%]	Lithotype with finely crystalline pyrite	Tendency to selfignition
				Vt	L	I			
1	Cheluskintsev, l_4	LRC	0.71	87	8	5	2	5	non-prone
2	Trudovskaya, l_4	LRC	0.55	86	5	9	11	6	prone
3	Kurakhovskaya, l_4	LRC	0.66	89	7	4	3	0	—
1^1	Ukraine, k_8	RC	0.57	83	6	11	11	50	non-prone
2^1	Trudovskaya, k_8	RC	0.49	80	8	12	4	54	prone
3^1	Kurakhovskaya, l_2'	RC	0.52	80	9	11	7	63	—

Table 3

Characteristics of weakly reduced and reduced coals and their semi-cokes, [%]

Sample	Type	A^d	C^{daf}	H^{daf}	H/C, [atm]	S_t^d	S_o^d	S_p^d	S_s^d	Yield of semi-coke	Surface*, [mg/g]
Original coal No 3	LRC	5.3	79.30	5.07	0.77	1.04	0.85	0.07	0.12	—	—
Semi-coke		24.2	84.19	2.35	0.33	0.79	0.73	0.02	0.04	77	466
Original coal No 3^1	RC	8.6	76.10	5.22	0.82	5.60	3.14	2.44	0.02	—	—
Semi-coke		20.0	84.65	3.47	0.49	1.60	1.06	0.48	0.06	62	193

* by iodine

Desulphurising effect of thermal treatment was registered. The content of S_t^d, S_o^d and S_p^d sulphur decreased more essentially during pyrolysis of RC samples (Fig. 3).

Infrared spectroscopy with DRIFT techniques was applied for semi-quantitative evaluation of chemical changes associated with influence of steam pyrolysis on coal structure. DRIFT data gave us basis to assume that thermal treatment of all samples causes the appreciable decrease in the relative intensity of the absorption bands of 1200 cm^{-1} (C–O–), 1050–1070 cm^{-1}, 1440 cm^{-1} (CH$_{al}$) in semi-cokes (Table 4, 5). These changes are more pronounced in LRC samples.

Table 4

Relative intensity (I_x/I_{1600}) of the selected regions of the DRIFT spectra for investigated coals and semi-cokes

Sample	Type	C = O 1650	C–O– 1200	1050– 1070	Chal 1440	CHar(1H) 860–880	CHar(2H) 820–830	CHar(3,4H) 760–780
Original coal No 3	LRC	0.27	0.41	1.56	0.81	0.84	0.87	0.57
Semi-coke		0.35	0.05	0.02	0.03	0.13	0.11	0.09
Original coal No 3[1]	RC	0.24	0.71	2.12	1.01	0.70	0.75	0.60
Semi-coke		0.24	0.43	1.67	0.32	1.25	1.13	1.05

Table 5

The changes of sample characteristics after thermal treatment

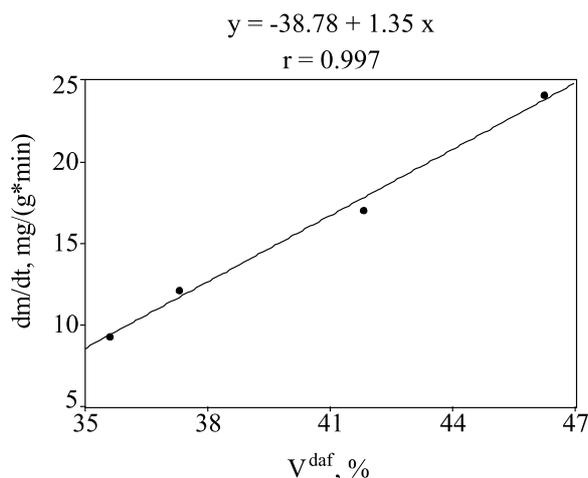| No	Type	Ultimate analisis, [%]					DRIFT data, $\Delta(I_x/I_{1600})$ at regions, [cm^{-1}]				
		$\Delta H/C$, [atm]	$\Delta(O+N)^{diff}$	ΔS_t^d	ΔS_o^d	ΔS_p^d	1650–1670	1200	1050–1070	1440	860–880
3	LRC	0.40	1.92	0.25	0.12	0.05	–0.08	0.35	1.54	0.77	0.71
3[1]	RC	0.33	2.80	4.00	2.08	1.96	0.00	0.28	0.45	0.69	–0.55

$$y = -38.78 + 1.35\ x$$
$$r = 0.997$$

Fig. 5. Maximal rate of mass loss as a function of V^{daf}

The main differences between RC and LRC semi-cokes are that the RC partners enrich by all kinds of the CH$_{ar}$-groups.

Table 5 shows a strong variation in the heteroatoms content and relative content of functional groups of coals after thermal treatment. It can be seen from the table that heteroatoms losses for LRC coal type happened predominantly on account of oxygen losses, and for RC — predominantly on account of sulphur losses. At the same time, the LRC desulphurisation is the result of predominant removal of S_o, and desulphurisation of RC — the result of S_o+S_p removal.

Therefore, C–O–, –S–S–, CH$_{ar}$, CH$_{al}$ bonds dominate in the semi-cokes from RC (Table 4), i.e. their structure is more laced what corresponds to the agglutinate material.

In contrast, the aforementioned bonds, destroyed during LRC heating, created the semi-cokes with high value of specific surface area (Table 3).

Coals under investigations were subjected to thermal treatment with the aim to study the influence of genetic coal type on its tendency to self-ignition. The corresponding curves, plotted on the bases of thermogravimetric data, are given in Figure 4. From the curves, it can be seen that the maximal gas evolution rate increases in the series: LRC > LRC* > RC > RC*.

Pyrolysis of coals tended to self-ignition resulted in a 1.8–2.0 — fold acceleration in the maximal gas evolution rate.

The presence of linear proportional relation between the maximal rate of mass loss and yield of volatile matter has been observed. Figure 5 shows the graphical representations of regression modelling results.

CONCLUSIONS

The experimental data allowed to establish some differences in the structure and properties of LRC and RC coals, based on their behaviour during thermal destruction. There are differences in the quality of active sites involved in coals thermo-destruction process. These sites, first of all oxygen and sulphur bridges, play one of the most important roles in pyrolysis.

Semi-cokes from RC are rich in sulphur and oxygen bridges. They have agglutinate structure. In contrast, the afore-mentioned bonds, destroyed during LRC heating, created the powdered semi-cokes with high value of specific surface area.

It was shown that LRC and RC coal types differ in the elements composition, especially in oxygen and sulphur content, and in the kinetics of its thermal destruction process.

Pyrolysis of coals tended to self-ignition resulted in a 1.8–2.0 — fold acceleration in the maximal gas evolution rate.

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