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ENNOBLING OF SALTY COALS BY MEANS OF OIL AGGLOMERATION

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Abstract. The phenomenon of coal modification at oil agglomeration has been studied, specifically, changing of its structure and physical-chemical properties of surface. It was established: - agglomeration process of coal with size 0-1(3)mm is accompanying by direct adhesive contact of "coal-oil" on 75-80 % from external surface of coal. The high power chemical bonds are formed together with physical bondes in the interphase zone. This modification leads to the increasing hydrophobicity of coal surface and the contrastance of mosaic liophylic-liophobic picture; - internal surface of coal is hydrophobized by diffusing oil agent into pores and fissures. Infiltration phenomenon intensifies this process since light fractions of a binder penetrate into micropores of coal substance; - the changes in supermolecular structure of coal organic mass (COM) have been revealed in oil agglomeration process.
The experience carried out on low rank salty coals of Western Donbas.

Keywords: Oil agglomeration, coal structure, specific modification, adhesion.

Introduction. Perspective of exhausting natural reserves of petrol and gas and increase of coal consumption have conditioned an increasing interest of the world scientists to coal technologies. Special attention is given today to the study of special processes of coal preparation and ennobling, and this opens new possibilities of processing of low grade raw materials to conditional ecologically clear products [1].

During past ten years the process of coal selective oil agglomeration is quickly developed. The interest to this problem is considerable not only from specialists in fossils ennobling, but also coal chemists, heat-power engineers, transport workers [2-5]. The oil agglomeration is considered by us as a perspective high efficient substance of preparing low quality coal to coking, burning, pyrolysis and also as polyfunctional process of coal preparation to its liquefaction. Besides, some investigators have demonstrated advantages of utilization the techniques and technologies of oil agglomeration in main hydrotransport systems of energetic and coking coal [6,7].

Universality and technological parameters of oil pelleting allow to use it for processing of low grade coals, in particular, oxidized, with high ash, and high salt content (salty coals).

The goals of our investigation were: to study the structural changes of coal organic mass (COM) at its oil agglomeration; to estimate the efficiency of oil pelleting using for obtaining ecologically suitable coal products.

Experimental.

Primary raw materials and reagents. Energetic and coking coals from Donetsk (UKRAINE) are of different rank with ash content from 10 to 14 %, have been investigated [2]. Special attention was given to salty coals (SC) of Novomoskovskoe deposit, Western Donbas. The some characteristics of this sample are, %: $\mathbf{W}^{\mathbf{a}}$ = 21,4; $\mathbf{A}^{\mathbf{d}}$ =9,9; $\mathbf{C}^{\mathbf{daf}}$ = 72,8; $\mathbf{H}^{\mathbf{daf}}$ = 5,0; $\mathbf{V}^{\mathbf{daf}}$ = 42,6 **.** Na_2O content in ash is 11,6 %. The furnace residual oil (mazut M100), oil of oiling charge (OOC) and polymer of benzene department of coke-chemical production have been used (as reagents-binders).

Parameters of oil agglomeration process: Agglomeration process has been carried out in the laboratory granulator of impeller type at solid : liquid=1:3, pH=7, t = 18-20 ^{o} C, frequency of impeller rotation 1500 min^{-1}, concentration of binder was from 3-5 to 25-30 mass. %, size of coal particles were from 0 to 200 mn.

Methods of investigation:

- Optical microscopy of agglomerates (microscope NEOPHOT-21);
- Electron parametric resonance (radiospectrometer RE-1306);
- IR-spectrometry (Specord IR-75, Perkin-Elmer);
- X-Ray diffractometry (DRON-UM-1,5);
- Photocolorimetric studying of coal surface.

RESULTS AND DISCUSSION.

Microscopic investigations of coal-oil structures anshliffs (flocules, agglomerates, granules) allowed to select 4 principal structure types of coal aggregates (fig. 1):

I - *pellicle* - compact formations, with thin broad pellicles of oil-binder between individual grains of coal.

II - *meniscus*- structures with concave meniscus of binder between coal grains on aggregates surface.

III - *powdered*- when binder drops filled with coal grains.

IV - *bridge* - friable formations of coal grains, which are bonding with oil-binder “bridges”.

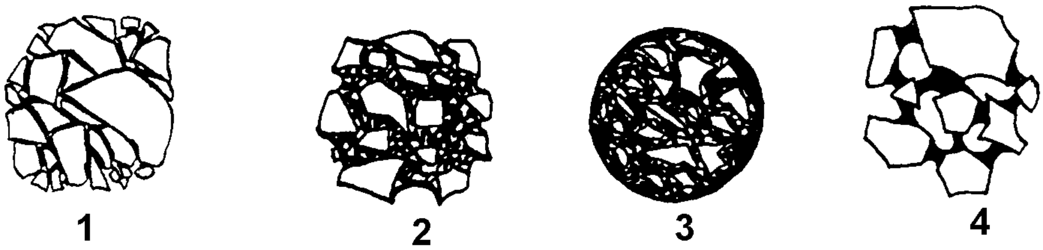
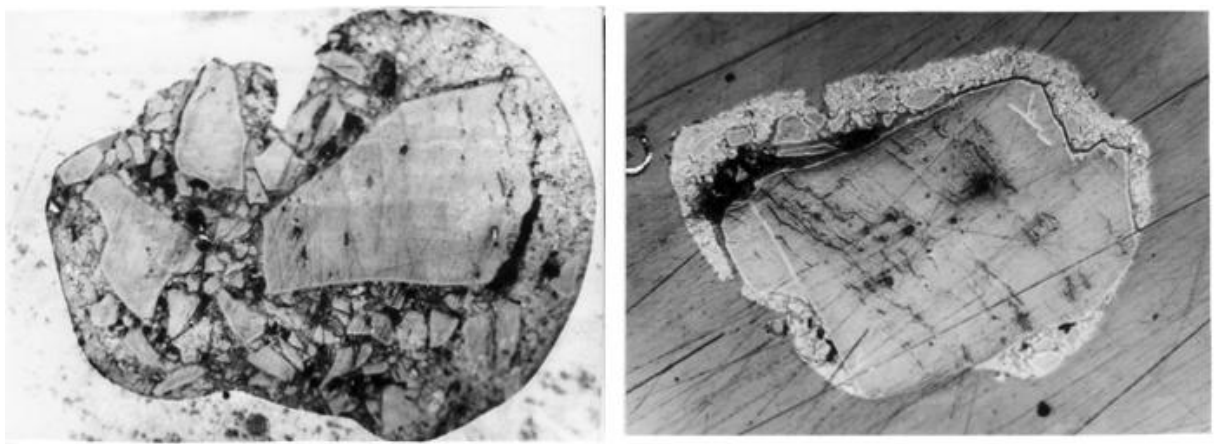


Fig. 1. Oil-coal agglomerates (x 5 times)

With photocolorimetric methods (using methylene blue solution) [8] has been established the part of coal grains surface, which are cowed with a binder for the I type structures consist of 57-79 %, II - 86-95 %, III - 100%, IV - 40-44%. This case on the coal grains surface of I type oxi-pellicle ("white border" around coal grain) can be kept; it doesn't exist in III rd type of granules (fig.2).

I type (a,b)



III type (c,d,)

Fig.2. Anshlifs of granules: I type (a, b) - x600; III type(c,d,) - x400.

However, for salty coals that high parameters are achieved only at special treatment of raw material with oil agent.

In general, the salty coal has a hydrophilic surface and it is agglomerated by apolar agent with difficulty. To increase its agglomeration capacity, we have worked out a number of steps.

Firstly, this is oil treatment of coal (with mazut M100, for exemple) during the crushing process [9].

Secondly, for salty coal agglomeration, it is recommended to use aromatized agents which contain functional oxygen groups in the side links [10].

Thirdly, the agglomeration process itself should be carried out in conditions of increased turbulance of water-coal-oil mixture (Re > 3000) and Solid: Liquid = 1:1(3). Without special treatment of coal surface, cowing with the binder is fluctuated between 0-5 % only. This fact can be interpretated as a low natural ability of SC to agglomeration.

Microscopic investigations allow to confirm a penetration of a binder in pores and fissures of coal substances (fig.3). It is obviously, that this process is accompanied by infiltration phenomena, during which light fractions of binder penetrate into micropores and more heavy ones remain on surface of coal grains. The last one promotes the formation of border solvate layer of binder on coal surface.

Fig. 3. Anshlifs of oil-coal granules with the penetration of oil into coal substance x600

As the result, the cohesion of binder pellices is arised, and the stability of aggregates (agglomerates, granules) is increased.

Paramagnetic characteristics of samples were determined on serial radiospectrometer RE-1306 at wave length λ = 3,2 sm in air. Mn^{+2} in a lattice of MgO was the internal standard.

The obtained data for constituents of agglomerate, intermediate and end products are shown in table 1. It is seen, that the first addition of oil agent (I stage of process) did not influence on nature and paramagnetic centers (PMC) concentration significantly.

Oil-agent M 100 is more complex, because its three types of PMC are characterized. They are very differed from one another (Fig. 4).

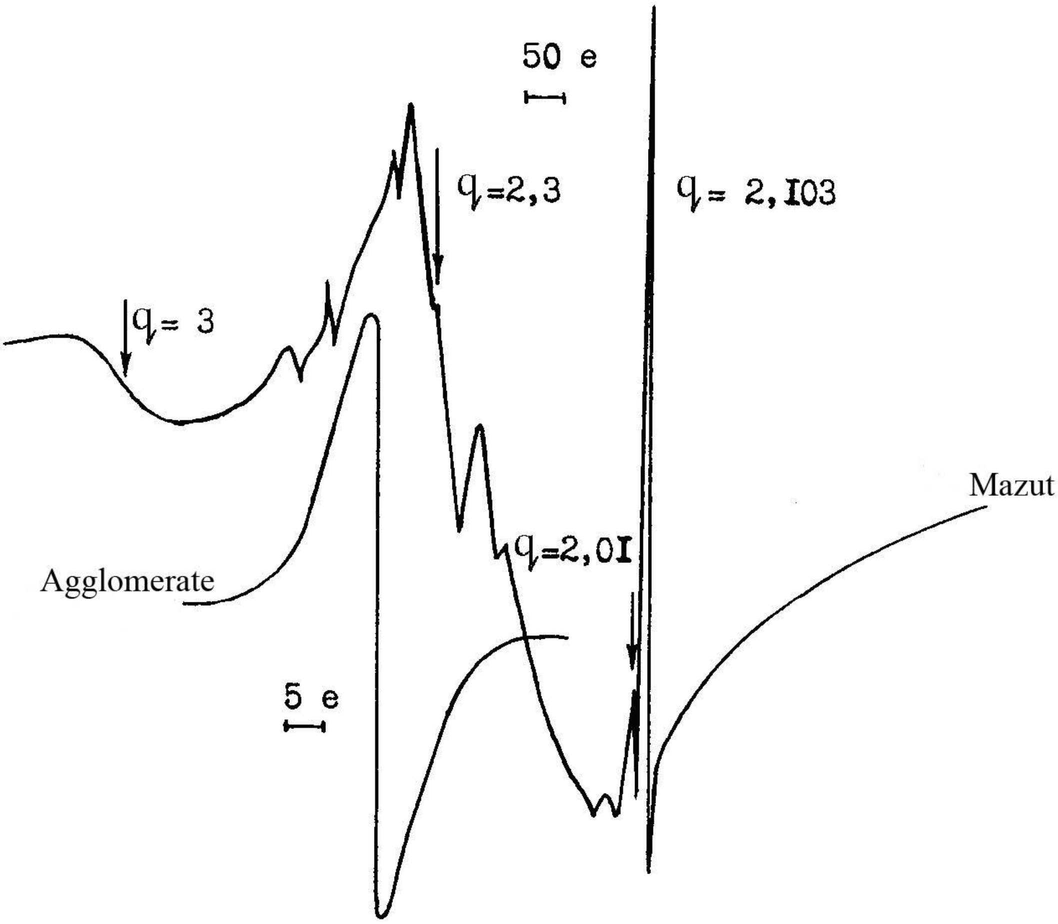


Fig. 4. ERS-spectra of M100 and agglomerate, which has been obtained on the basis of salty coal (Novomoskovskoe deposit, Western Donbas).

Table 1

Sample	ΔH , Gs	g-factor	N, spin/g
Initial coal	4,6	2,0035	$8,9.\ 10^{17}$
Coal +5% mazut:			
In air	4,6	2,0036	$8,9.\ 10^{17}$
In vacuums	4,9	2,0036	$9,8.\ 10^{17}$
Mazut:			
Signal 1	4,6	2,0031	$9,7.\ 10^{16}$
Signal 2	12,4	2,0169	$9,7.\ 10^{16}$
Signal 3	320	4	$9,7.\ 10^{16}$
Agglomerates			
Agglomerate - 23	4,8	2,0035	$1,4.\ 10^{16}$
Agglomerate - 29	5,1	2,0035	$4,8.\ 10^{16}$

Literature data analysis allowed to classify signal I (at g = 2,0031 and ΔH = 4,6 e.) as π-polyconjugated systems [11], signal II (with g ~ 3-4 and ΔH = 320 e.) as ferrum-containing paramagnetic structures [12], but signal III (with g ~ 2,017 and Δ H ~ 12 e.), perhaps, as radicals of peroxide (R-O-O) or R - S - S [13] types.

PM-characteristics of agglomerates A-23 (% of mazut) and A-29 (% of mazut), as it was expected, are more similar to same of parent coal, excluding PMC concentration. The last one is lower. It is testified about chemical interaction between coal and oil, or, at any rate, about sharply change of intermolecular interactions into COM. Evidently in this case, the important role belongs to water, as a strong hydrolyzing agent .

If it is so, the changes in supermolecular organization of COM and in active oxygen-containing group's composition must take place. As has been established (Table 2), in the agglomeration process of SC carboxyl and quinone groups decreasing and phenol hydroxyl increasing happened. Besides, the significant lessen of sodium concentration takes place, that is to say, desalting raw material to conditional level (Na_2O in ash < 2 %).

Table 2

Sample	Oxygen-containing groups, mg-ekv/g			Na - contain, mg-ekv/g		Heat of combustion Q, MJ/kg
	OH	COOH	O=N=O	in coal	in ash	
Initial coal	1,60	0,20	9,3	0,30	4,08	24,3
A-23	2,44	0,11	7,1	0,10	1,77	28,2
A-29	2,40	0,10	6,5	0,10	1,88	28,6

Evidently the annihilation of ERS signal II of M 100 (g-factor ~ 3-4; H ~ 320 e.) and quinone concentration decreasing, , are connected between one and another. We admit, that formation of helate complexes take place here, the central ion is Fe^{3+}, and the ligands are electron donor quinone structures.

The phenol groups increasing can be explained with particular quinones reduction by proton donor structures of oil or by hydrolysis of salt form (phenolates) during agglomeration process, which include the water treatment stage.

The decreasing of free carboxyl groups concentration may be explained with their particular substitution by metal or strong H-bonds formation (IR-spectra, fig. 5).

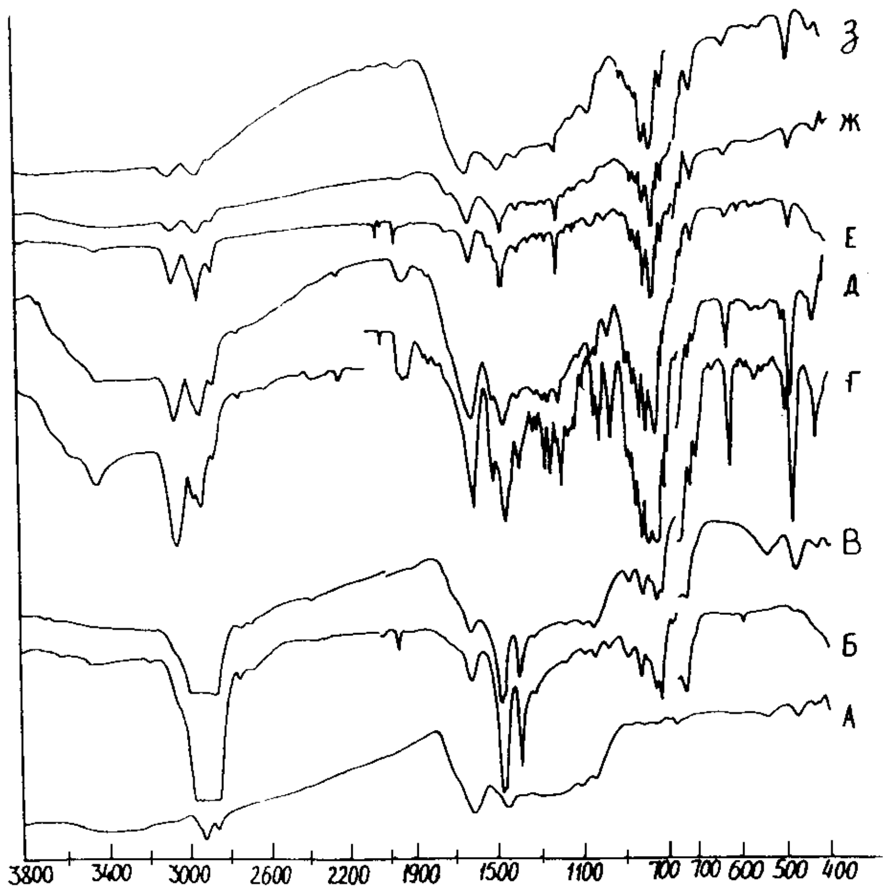


Fig. 5. IR-spectra of oil-coal aggregates and their components: а - coal of mine “Inskaja”, sort G; б - M100; в - agglomerate ”M100-coal”; г - OOC; д - agglomerate “OOC-coal”; е - polymer; ж - aggregate “polymer -coal”; з - same agglomerate after 10-days keeping on air.

These conclusions are confirmed by IR-data and X-Ray investigations, which we are going to be published in the next article.

CONCLUSIONS:

During oil agglomeration of coals radical changes of physic-chemical surface characteristics of coal substances take place. They are caused by interphase interaction "coal-oil". That is why it can wait sufficiently different technological properties of agglomerated coals and parent coals.

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