THE CHEMICAL PLANTS WASTEWATER UTILIZATION AS A SOURCE FOR THE WATER-COAL FUEL PRODUCTION

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Abstract: *An influence of components of the chemical coke refinery wastewater on properties of the highly concentrated water-coal suspensions (HCWCS) (also produced from the coke refinery solid wastes) has been investigated. It has been shown that this wastewater can be used in production of HCWCS – a new ecologically safe fuel for the thermal electric powerplant boilers.*
Almost any wastewater with organic substances contamination (including food industry wastewater) can be used as a dispersion media for obtaining of HCWCS.

Keywords: *coke refinery wastewater, highly concentrated water-coal suspensions, organic substances contamination.*

Coal is one of the most important sources of the thermal energy for various branches of industry. It is practically one domestic source of energy in Ukraine with hundreds years lasting prospects. It feeds thermal electric powerplants, railway and water transport and also various household needs. Coke refinery industry requires significant amount of the high grade coal, which is quite deficient. This fact raises attention to the coal refinery slurry, flotation wastes and other coal-containing waste materials. It is known that mosaic distribution exists in the slurry collecting lakes both in vertical and horizontal direction. Selected areas of the lakes may contain coal materials with ash content of 35-45 % or 45-55 %. Such materials can be used in various branches of energy production even without any significant technology changes [1-4, 6].

There are 64 coal refinery plants with "wet" refining technology in Ukraine. This technology causes formation of technological wastewater containing from 80 to 150 g/l of the coal and empty material particles. The plant with incomplete technological cycle can produce slurry containing 35-45 or lower wt % of ash, which can be sold as a side technological product. Processing of such slurry comprises stages of precipitation in the external slurry lakes, excavation and drying of the slurry followed by its delivering to the thermoelectric powerplant. This technological flowchart can be used all year around but winter.

Floatation wastes and highly ash containing fugates can contain of 50-100 g/l of the solid phase and should be piped (sometimes transported using specialized cargo trucks) to the slurry collecting lakes. Drainage wells or bottom water collecting system should be installed there to collect cleared water from the lake. This water can be discharged to the natural water objects or recycled in the plant's technological cycle. However, special attention should be paid to the suspension and phenols content in this water. Cleared water way should be constructed to ensure longer way to the discharge point in order to achieve more complete precipitation of the solid pollutants. Special pond for the atmospheric precipitations should also be constructed at the wastewater collecting area. Total amount of the coal refining slurry in Ukraine is estimated as more than 100 million tons and their area is more than 3000 hectares.

Highly water containing technological wastes are very dangerous especially at the natural disasters. They also require rather high maintenance expenses [5-7]. Reuse and recycling of the coal industry wastes has become very acute problem in Ukraine. Solid wastes can be recycled in many construction, building and roadworks.

Thus, waste materials from 35 coal refining factories are being reused as source materials for the wall building materials, agloporous sand and macadam, bricks, drainage pipes, fuel-technological admixture for the clay materials, agriculture fertilizers and prophylactic mud accumulation.

However, possible recycling of such waste materials as secondary energy carrier in the coke refining industry still needs further elaboration.

Results of many works prove that coal mines, coal refining slurry and solid wastes of the coke refining industry can be very promising materials for industrial recycling. This issue becomes especially important because of current reducing of the primary coal production in Ukraine.

Current technologies ensure production of the coal concentrates with ash content of 10-30 % from the source material of 30-40 % ash content. However, they do not ensure complete extraction of all needful slurry components resulting in formation of new waste materials.

Utilization of industrial, first of all coke refining wastewater from mud and slurry collectors becomes very important problem. Current decontamination technologies still require high material and finance expenses [8-11].

Industrial wastewater should satisfy following conditions in order to enable utilization as a dispersion medium of HCWCS:

- polluting impurities should not evaporate from the surface;
- present impurities should not negatively influence characteristics of HCWCS (rheological properties, sedimentation stability);
- HCWCS should burn completely emitting no ecologically dangerous components.

This project was aimed onto investigation of possible ways of utilization of industrial wastewater in production of the water-coal and slurry-coal suspensions.

We worked with solid waste materials of Yasinovo coke refinery (W^d = 15 %, A^d = 23 %), and wastewater after preliminary cleaning. Sodium lygnosulfonate with NaOH was used as a plasticizing agent [12, 13]. A steel balls grinder (volume 1,3 l, ball diameter 28 and 10 mm) was used to grind the source material. Grinding should last until lowering of 250 µm particles below 0.1 wt %. This required about 35 minutes at 35 rpm. Longer grinding time resulted in significantly higher viscosity of the system (probably because of higher content of the fine disperse clay particles). All grinding were performed under single stage procedure. Investigation of influence of the plasticizing agent content on the suspension properties proved that 1.0-1.1 % of the agent results in decreased viscosity of the system. Lower concentration of the agent is still insufficient to achieve this effect while further raise of the agent content do not result in any significant viscosity lowering. Slurry-coal suspension may be temporarily stored in the static conditions before burning. Therefore, it should be important to research time changes in their rheological parameters and sedimentation stability.

All the systems were thoroughly mixed before any measuring to avoid possible gravitational size distribution of the particles. Viscosity of the disperse systems was measured immediately after grinding and in 2, 24, 48 and 120 hours after static storage of the suspensions using "Rheotest-2" and at the shifting speed from 1 to 437.4 c^{-1} through the standard methodic. Sedimentation stability was measured as time elapsed until layering of the suspension followed by separation of the clear liquid without solid particles on surface of the suspension. We analyzed slurry-coal suspensions containing of 59, 61, 63 and 65 wt % of the disperse phase. The higher is concentration of the disperse phase, the higher will be viscosity of the system (see Fig. 1).

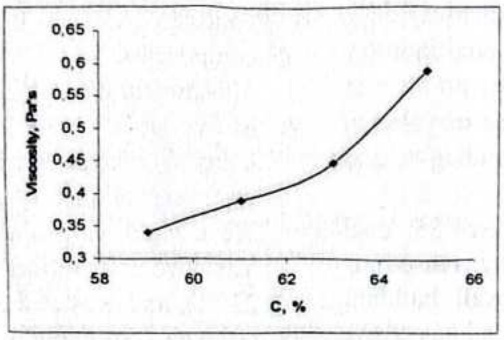

Figure 1 Dependence of the slurry-coal suspension viscosity on the solid phase concentration.

64-65 wt % is the critical concentration and viscosity of the system gets steeper rise after this point. Rheological analysis of the slurry-coal suspensions proved that they can be piped using wide range of the transportation speed and shifting tensions (see Table 1).

Table 1 Rheological characteristics of the slurry-coal suspension based on slurry and wastewater of Yasinovo coke refinery ($C_{s.p}$=63%)

Speed gradient, D_r, s^{-1}	*Suspension storage time, hour*									
	0		*2*		*24*		*48*		*120*	
	τ, Pa	*η, Pa*s*	*τ, Pa*	*η, Pa*s*	*τ, Pa*	*η, Pa*s*	*τ, Pa*	*η, Pa*s*	*τ, Pa*	*η, Pa*s*
1	0,9	0,9	0,81	0,81	0,9	0,9	1,02	1,02	1,18	1,18
1,8	1,51	0,84	1,66	0,92	1,81	1,01	2,05	1,14	2,34	1,3
3	1,81	0,60	2,1	0,7	2,41	0,8	2,79	0,93	3,24	1,08
5,4	2,41	0,45	2,97	0,55	3,62	0,67	3,78	0,7	5,3	0,98
9	3,92	0,44	4,5	0,5	6,03	0,67	6,66	0,74	8,1	0,9
16,2	6,03	0,37	7,45	0,46	9,05	0,56	11,12	0,69	13,45	0,83
27	8,74	0,32	11,88	0,44	15,38	0,57	18,1	0,67	21,6	0,8
48,6	13,87	0,29	18,95	0,39	25,33	0,52	30,1	0,62	36,9	0,76
81	21,11	0.26	29,2	0,36	40,4	0,5	47,8	0,59	56,7	0,73
145,8	33,17	0,23	48,11	0,33	65,73	0,45	81,6	0,56	102,1	0,7
243	45,23	0,19	72,9	0,3	97,03	0,4	131,2	0,54	165,2	0,68
437,4	71,99	0,16	122,5	0,28	169,0	0,39	218,7	0,5	284,3	0,65

Higher shifting speed causes viscosity lowering and dependence of viscosity on the shifting speed becomes linear at speed values of $10s^{-1}$ or higher (Fig. 2).

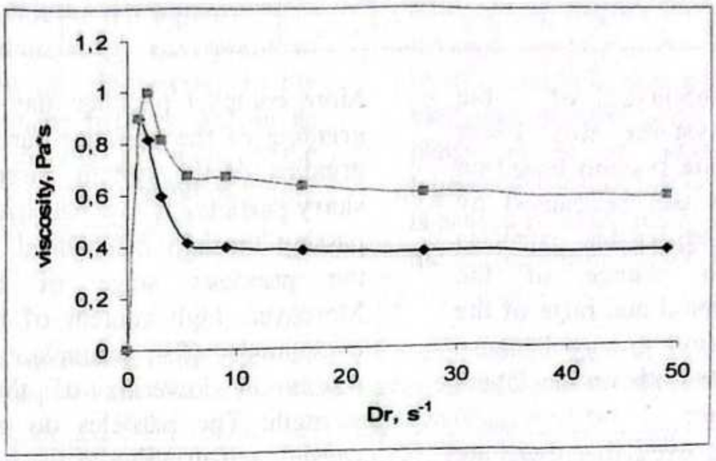

Figure 2 Dependence of viscosity of the suspension based on slurry and wastewater of Yasinovo coke refinery ($C_{s.p}$ =63 %) on the shifting speed

1 – fresh made suspension
2 – after 24 hour of storing

The suspensions start to exhibit characteristics of the Newtonian liquid at higher shifting speed because of destruction its inner structure. Gradual lowering of the tension leads to restoration of the disperse system spatial structuring. However, the system returns to its initial state at other path (Fig. 3).

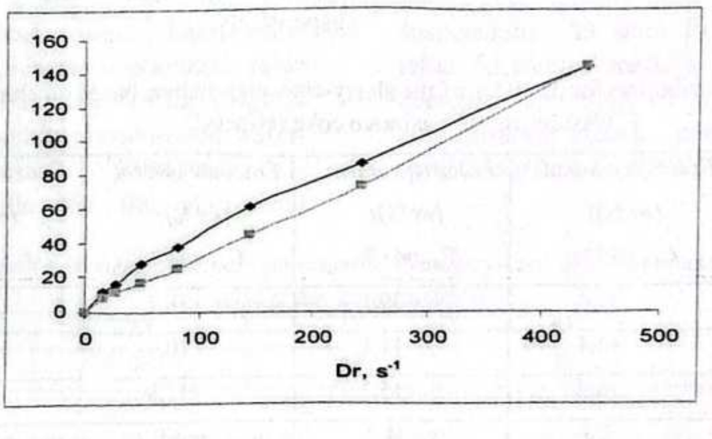

Figure 3 Hysteresis path for the suspension based on slurry and wastewater of Yasinova coke refinery ($C_{s.p}$ =63%)

1 – tension speed raises ;

2 – tension speed decreases.

As seen from the Table 2, sedimentation stability of the disperse systems raises at increase of the disperse phase concentration. This effect is probably caused by more compact packing of particles in the system.

Table 2 Dependence of the sedimentation stability of the slurry-coal suspensions based slurry and wastewater of Yasinovo coke refinery on the solid phase concentration.

C, %	59	61	63	65
Sedimentation stability, days	4	4,5	4,5	5

Sedimentation stability of the wastewater-based systems was lower comparing to the same systems based on the tap water. This can be caused by formation of the aggregated particles complexes due to change of the electrokinetic's potential and raise of the interparticle interaction energy because of formation of dense adsorption layers on the particles surface.

Our investigations proved that there are two factors ensuring raise in the system's viscosity: increase of the solid phase volume content and change in its granulometric compositions.

Raise of the solid phase content at the grinding causes more intense dispersion of this phase and increase of the finely dispersed particles content.

As seen from the Table 3, size distribution approaches to the mono-modal mode.

More compact packing may cause self-grinding of the particles during external grinding of the system. Strength of the slurry particles is low because they were passing through mechanical grinding at the previous stage of enrichment. Moreover, high content of the mineral compounds (for example, clay) also results in lowering of the particles strength. The particles do not interact causing self-grinding at the beginning of grinding if the solid phase concentration is comparatively low.

Higher concentration leads to more intense interaction between the particles and finer grinding. Shorter grinding time would be expedient to keep the bimodal granulometric composition however, bigger particles of 250-400 μm would remain in the suspension. This is inappropriate for the slurry-coal suspensions.

Table 3 Size distribution for particles of the slurry-coal suspensions based on slurry and wastewater of Yasinovo coke refinery.

Fractional limits, (d, μm)	*Fraction content (wt %); $C_{s.p.}$=59 %*	*Fraction content (wt %); $C_{s.p.}$=61 %*	*Fraction content (wt %); $C_{s.p.}$=63 %*	*Fraction content (wt %); $C_{s.p.}$=65 %*
250 – 100	40,4	39,1	38,3	34,3
100 – 80	14,4	11,1	10,9	8,3
80 – 40	16,2	15,3	17,8	16,3
40 – 30	5,3	4,7	6,2	4,9
30 – 20	7,2	8,7	8,2	9,7
20 – 10	6,2	4,2	7,8	9,0
10 – 5	4,1	5,3	3,2	7,6
5 – 2	4,1	5,3	2,1	5,5
2 – 1	1,1	5,1	2,4	2,9
1 – 0	1,0	1,2	3,1	1,5

Grinding with the wastewater results in obtaining finer slurry particles comparing to the grinding with the tap water.
This can be caused by adsorption of admixtures from the wastewater in the particle pores, micro fissures and on its surface, which results in raise in the splitting pressure of desperation of bigger particles and their aggregates [14, 15].

Electrokinetic's characteristic of the disperse phase particles is one of the determining factors for properties of the disperse systems. As seen from our results, electrokinetic's potential of both clay and organic parts of the disperse phase raises at adding of sodium lygnosulfonate. In our opinion, this effect is caused by effective dispersive action of the reagents used (Table 4).

Table 4 Dependence of the electrokinetic's potential of the disperse phase particles for the slurry-coal suspension based on slurry and wastewater of Yasinovo coke refinery on the plasticizing agent concentration (C_{solid} = 63 %).

Plasticizing agent concentration, kg/m³	*Electrokinetic's potential for the clay particles, mV*	*Electrokinetic's potential for the coal particles, mV*
0,02	22	34
0,04	24	35
0,06	26	37
0,08	31	39
0,10	35	42
0,12	36	44
0,14	40	46
0,16	42	47
0,18	42	48

We have found direct interrelation between electrokinetic's potential value and specific surface area of the disperse phase for the highly concentrated water-coal suspensions. However, this interrelation fails for the slurry-coal suspensions. As seen from the data of table 5, electrokinetic's potential value decreases at raise of the solid phase concentration (and, consequently, its specific surface area).

Table 5 Dependence of electrokinetic's potential of the slurry-coal disperse phase particle on the solid phase concentration.

$C_{solid\ phase}$, %	59	61	63	65
ξ, mV	46	44	42	39

This effect can be caused by formation of the compact particles aggregates containing comparatively big organic particle in the centre surrounded with finely disperse clay particles. Various particles charges can be cross-screened resulting in lowering of the total charge of an aggregate. This effect (decrease of the electrokinetic's potential) is unwanted since it causes higher possibility of further aggregation leading to lower sedimentation stability.

Highly concentrated slurry-coal suspensions are intended to be used as a fuel for energy plants. That is why high combustion heat and deep burnout ratio are main requirements for such fuel. We have calorimetrically determined heat of combustion for samples of the source slurry, slurry-coal suspensions made with the tap water and wastewater from

Yasinovo coke refinery. Concentration of the solid phase in the suspensions was from 63 to 65 wt %. Table 6 represents results of this stage.

Table 6 Heat of combustion (kJ/kg) for the Yasinovo coke refinery slurry and slurry-water suspensions.

Fuel type	*Heat of combustion,kJ/kg*
Coke refinery slurry	**33491,8**
Slurry-coal suspension (with tap water), C_{sp} = 63 %	24372,1
Slurry-coal suspension (with tap water), C_{sp} = 65 %	25798,8
Slurry-coal suspension (with wastewater), C_{sp} = 63%	24492,3
Slurry-coal suspension (with wastewater), C_{sp} = 65%	25901,9

As seen from the Table 6, slurry-coal suspensions provide even higher heat of combustion value (recalculated to the dry fuel) comparing to initial coke refinery slurry. This effect is probably caused by deeper burnout degree in the suspensions (see Table 7). Besides that, water can promote process of burning. Wastewater-based suspensions ensure slightly higher heat of combustion value, which can be caused by presence of some combustible organic compounds in the wastewater.

Therefore, we can conclude that highly concentrated slurry-coal suspensions made from slurry and wastewater from Yasinovo coke refinery are advisable for use as a fuel. This way of utilization is economically and ecologically expedient even for other food and chemical industry wastewater, which contains organic pollutants. This wastewater can also become a source material for the liquid coal fuel production.

Table 7 Burnout degrees for solid slurry and highly concentrated slurry-coal suspensions.

Sample	*Sample weight, g*	*Dry compounds weight, g*	*Weight of combustible compounds, g*		*Weight of the ash after burning, g*	*Burnout degree, %*
			before burning	*after burning*		
Slurry of Yasinovo coke refinery	20	18,6	14,3	0,8	5,1	94,5
Tap water-based suspension (C_{sp} = 65 %).	30	19,5	15,1	0,05	4,45	99,7
Wastewater-based suspension (C_{sp} = 65 %).	30	19,5	15,1	0,09	4,49	99,4

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