- підвищити якість кінцевого продукту

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V.S. BILETSKY, Dr. Eng., Poltava National Technical University, Poltava, Ukraine, O.A. KRUT, Dr. Eng., Coal Power Technology Institute of the National Academy of Sciences, Kyiv, Ukraine, P.V. SERGEYEV, Dr. Eng., Donetsk National Technical University, Donetsk, Ukraine

THEORY OF HIGHLY LOADED COAL-WATER SLURRIES

It is demonstrated that the theory of highly loaded coal-water slurries (HLCWS) may be underpinned by an analysis of the energy state of the HLCWS solid phase with the use of basic assumptions of the aggregative stability theory of lyophobic dispersion systems (DLVO theory). Accordingly, an analysis of the energy state of the HLCWS solid phase was performed, which allows to clarify the nature of phenomena taking place with changes to the size and surface potential of coal and mineral particles as well as hydrophilous-hydrophobous balance of their surface.

Показано, що в основу теорії висококонцентрованих водовугільних суспензій (ВВВС) може бути покладено аналіз енергетичного стану твердої фази ВВВС із застосуванням фундаментальних уявлень теорії агрегативної стійкості ліофобних дисперсних систем (теорії ДЛФО). На цій основі виконано аналіз енергетичного стану твердої фази ВВВС, що дозволяє пояснити природу явищ, які мають місце при зміні крупності і поверхневого потенціалу вугільних і мінеральних частинок, гідрофільно-гідрофобного балансу їх поверхні.

Показано, что в основу теории высококонцентрированных водоугольных суспензий (ВВУС) может быть положен анализ энергетического состояния твердой фазы ВВУС с применением фундаментальных представлений теории агрегативной устойчивости лиофобных дисперсных систем (теории ДЛФО). На этой основе проведен анализ энергетического состояния твердой фазы ВВУС, что позволяет объяснить природу явлений, которые имеют место при изменении крупности и поверхностного потенциала угольных и минеральных частиц, гидрофильно-гидрофобного баланса их поверхности.

Problem definition and the present state of the art. In the context of tight fuel resources and changing pricing policy of oil and gas in Ukraine an increase of the coal share in the fuel and energy balance is becoming ever topical. Among promising technologies is the use of highly loaded coal-water slurries (HLCWS) as fuel. On the one hand, it allows producing stable transportable coal-water fuel (CWF) which may be burnt in boiler furnaces with no prior dewatering. On the other hand, this technology features much better environmental safety [1, 2].

Highly loaded coal-water slurry itself is however a complex object characterized by numerous physical and chemical factors which govern its aggregative and sedimentation stability as well as rheological properties.

High stability and fluidity of slurries are the result of their thixotropic properties. Specifically, according to DLVO theory, the inverse thixotropic restorability in turbulent flows is achieved due to coagulation of the disperse solid phase of slurry in the position of a so-called “second potential well” on the curves “combined interaction energy (Ec) – interparticle distance (h)” [3-5].

The analysis of research and publications. The theory of thixotropic liquid systems is based on the main provisions of colloid chemistry, formulated in publications [3, 4, 6, 7]. The theory of coal-water slurries is at the moment at the stage of accumulating empiric data and testing working hypotheses.

The aim statement. of this paper is to assess the basic properties of HLCWS and tendencies in their changes from the viewpoint of the modern stability theory of lyophobic dispersion systems (DLVO theory).

Presentation of the material and research results.

1. Application of DLVO theory as theoretical basis for HLCWS

The main factors governing the behavior of a coal particle in a coagulated structure are: the particle size, a hydrophilous-hydrophobous balance of the particle surface, the total and electrokinetic potential of the latter. The characteristics of a coagulated thixotropic coal-water system are generally governed by the “depth” E_{m2} and coordinate h_{m2} of the second potential well (Fig. 1) [4].

According to DLVO theory, the combined interaction energy E_c of two spherical particles in liquid has two constituents i.e. ion-electrostatic E_e and molecular-disperse (Van der Waals) E_d:

$$E_c(h) = 2\pi \cdot \varepsilon_o \cdot r \cdot \varphi^2 \cdot \ln[1 + \exp(-\chi \cdot h)] - \frac{A_r}{12h}, \quad (1)$$

where ε_o is the absolute dielectric permeability of water (ε_o = 7.26×10-10 F/m); r is the radius of spherical coal particles, m; φ is the potential of the diffuse double layer (DDL) on the coal particle surface, V; χ is the inverse Debye radius (the reciprocal value of the diffusion layer thickness δ), χ = 1/λ, where λ is the extension (length) of the diffusion layer DDL (for most cases $\lambda = 1\times10^{-8}$ m^{-1}); h is the distance between solid phase particles in slurry; A_r is the Hamaker constant, J.

The second potential well of the curve $E_c(h)$ exists because the curve $E_d(h)$ decreases as a power function whereas $E_e(h)$ does so exponentially, i.e. the latter decreases faster than $E_d(h)$ (see Fig. 1).

Let us consider the influence of the above factors on the nature of the curve $E_c(h)$. We will take the initial parameters of equation (1) for the purpose (1).

The variation range of the coal particle size (d) is assumed to be 10-100 μm, which corresponds to the main rational size range of the HLCWS solid phase [1, 2] and according to [5] corresponds to the size of coarsely dispersed objects of colloid chemistry. It should be noted that such a viewpoint is not flawless but no doubt it exists, at least for some fine grains of the indicated size range.

He variation range of the total surface potential of coal particles is assumed to be 20-100 mV according to [8, 9]. Due to the different hydrophilous-hydrophobous balance, the Hamaker constant (A_r) for the heterogeneous coal surface varies within $(0.5\text{-}3.5)\cdot10^{-19}$ J [4].

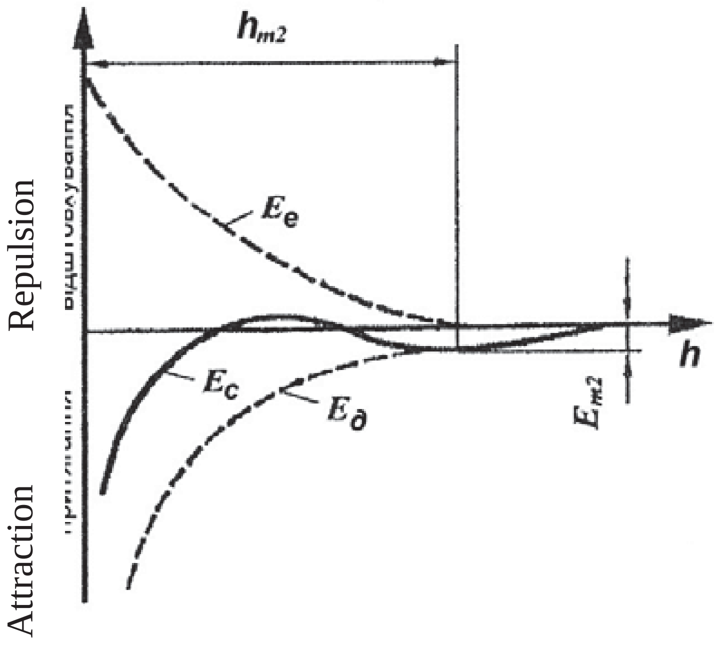

Fig. 1 Potential interaction energy curves of two particles as a function of their spacing

Fig. 2a shows the curves $E_c(h)$ for different coal particle sizes, obtained with the software MathCAD at the potential φ = 100 mV and the Hamaker constant $A_r = 3.5 \times 10^{-19}$ J.

As seen, the larger the size of coal grains, the higher the energy barrier of repulsion and at the same time the deeper the “second potential well”. The first of the above phenomena, the increased energy barrier of repulsion, results in the growing aggregative stability as the barrier prevents the particles from getting into and irreversible coagulation in the “first potential well”.

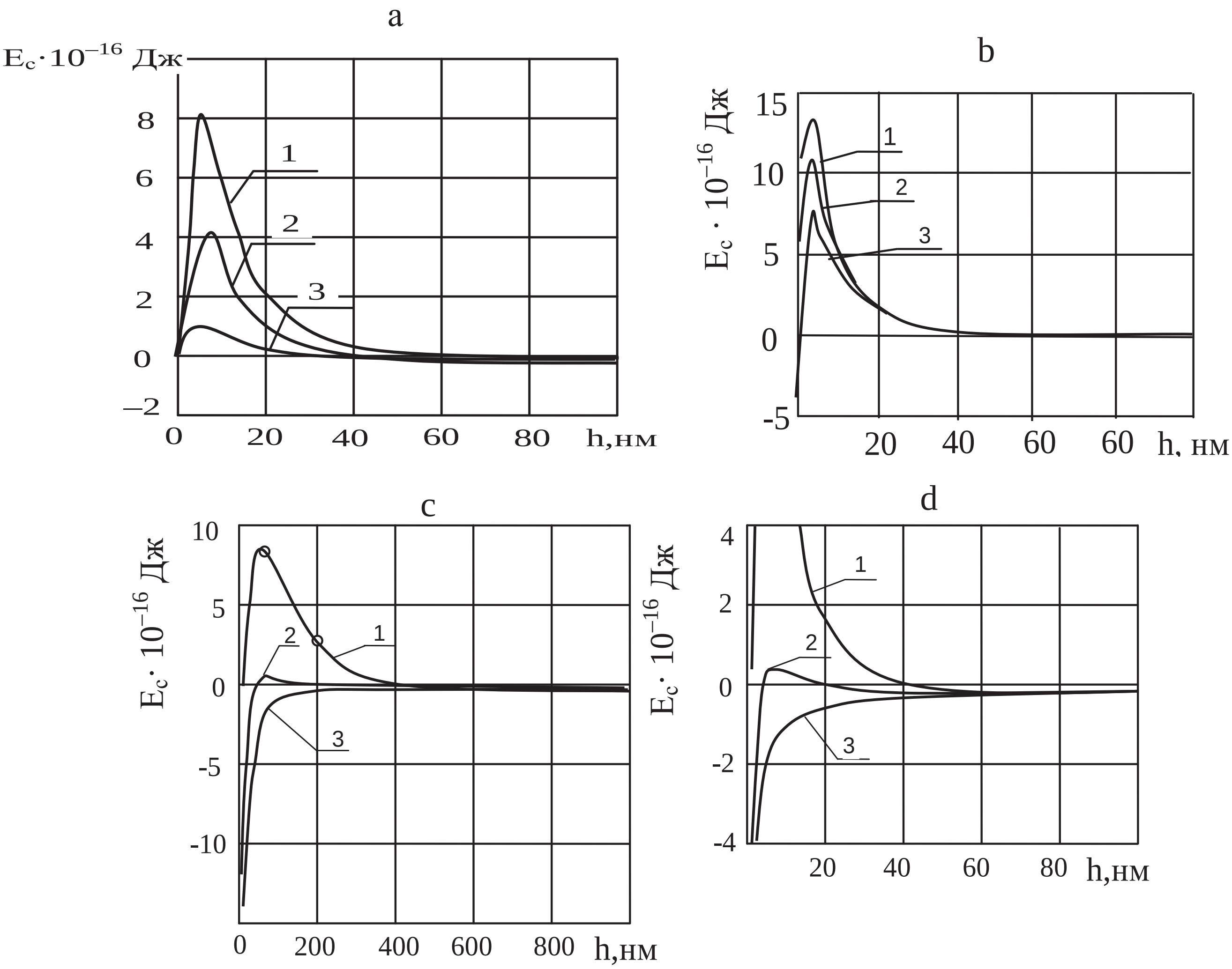

Fig. 2 Analytic dependences E_c (h) for coal particles:
a – with the size: 1- 100 μm; 2 – 50 μm; 3 – 10 μm.; b – at the changing hydrophilous-hydrophobous balance of the coal particle surface, the Hamaker constant: 1 - A_r = 0.5 •10-19 J; 2 - A_r = 1.5 •10-19 J; 3 - A_r = 3.5 •10-19 J; c, d – for the coal particle surface potential: 1 - 100 mV; 2 - 50 mV; 3 - 20 mV. (c – general survey scale of the curves; d – detailed against the axis E_c).

The second phenomenon, the deepening of the “second potential well”. contirbutes to a higer stability of the thyxotropic structure. The “deeper” this potential well, the higher the particle interaction energy in the reverse coagulation structures and the higher the HLVWS stability.

Now we will consider the influence of the coal surface heterogenicity factor on the energy state of HLCWS particles. In DLVO theory this heterogenicity (the hydrophilous-hydrophobous balance) is assessed with the help of the Hamaker constant (see equation (1)).

As is known [4], the stronger the coal phase interacts with water, the lower the Hamaker constant A_r is. Thie means that interparticle attractive forces get somewhat weaker. In other words, the increase of the constant Ar corresponds to stehgthening of the hydrophobous properties of the coal surface. The analytical curves $E_c(h)| A_r$ = var, $d_з$ = 100 μm, φ = 100 mV, which we obtained, confirm this thesis and show (Fig. 2b) that the growing hydrophobous properties of coal particles result in some decrease of the repulsion barrier height and hence in the reduced aggregative stability of HLCWS.

Figs. 2 c, d show the curves $E_c(h)$ for the total potential of the coal particle surface changing within 20-100 mV мВ at the coal grain size $d_з$ = 100 μm and the Hamaker constant $A_r = 3.5 \times 10^{-19}$ J.

An analysis of the obtained curves indicates that an increase in the potential of the coal surface gives rise to the energy barrier of repulsion which keeps growing. This barrier appears at $\varphi \approx 50$ mV. At $\varphi < 50$ mV coal-water slurry is aggregatively unstable. Under the influence of dispersive Van der Waals interactions, its grains irreversibly coagulate with each other and slurry laminates.

At $\varphi > 50$ mV there are two typical effects observed. Firstly, the repulsion barrier height significantly grows, which correspondingly increases the HLCWS aggregative stability. Secondly, the coordinate of the second power well h_{m2} shifts to the right. This results in a larger distance between coal particles which get retained in the second potential well of the thyxotropic structure. As a consequence, the water content of HLCWS for coal with a relatively large surface potential gets increased (and correspondingly its solid phase concentration is reduced).

2. Influence of the mineral constituent on HLCWS thyxotropic properties

Let us analyze the influence of the solid phase mineral constituent on HLCWS thyxotropic properties.

According to data [10], the mineral constituent of the Donbass steam coal that can be used for formulation of HLCWS is mainly represented by montmorillonite, kaolinite, hydromica and quartz.

It should be noted here that there can be several types of contact interactions identified in HLCWS as a thyxotropic structure: “coal grain – coal grain”, “mineral grain – mineral grain”, “coal grain – mineral grain”. Respective chains and space structures of these grains may form characteristic local zones in the HLCWS thyxotropic structure. The zones are represented only by contact interactions of the type “coal grain – coal grain”, covered above. Let us now consider contact interactions of the type “mineral grain – mineral grain”.

We will take the initial parameters of equation (1) for the purpose. The variation range of the mineral particle size (d) is assumed to be 1-10 μm, which corresponds to the actual size range of the HLCWS mineral component [5]. According to [11, 12], the variation range of the total potential of the mineral particle surface is assumed to be 40-200 mV. According to [12], the value of the Hamaker constant (A_r) for the hydrophilous mineral surface may be assumed to range $(0.2\text{-}2.0)\cdot 10^{-19}$ J.

According to [12], the inverse Debye radius χ does not depend on the surface charge density and the grain surface potential but is only a function of the charge of the DDL ions and their concentration. According to [12], the thickness of the diffuse double layer in case of mineral grains in water is within δ = 1-1000 nm. Correspondingly, the inverse Debye radius χ varies within 10^9-10^6 m^{-1}.

h, nm

Figs. 3 a, b show the curves $E_c(h)$ for different particle sizes at the potential φ = 100 mV and the Hamaker constant $A_r = 1 \cdot 10^{-19}$ J.

As seen, the energy barrier of repulsion and simultanepously the depth of

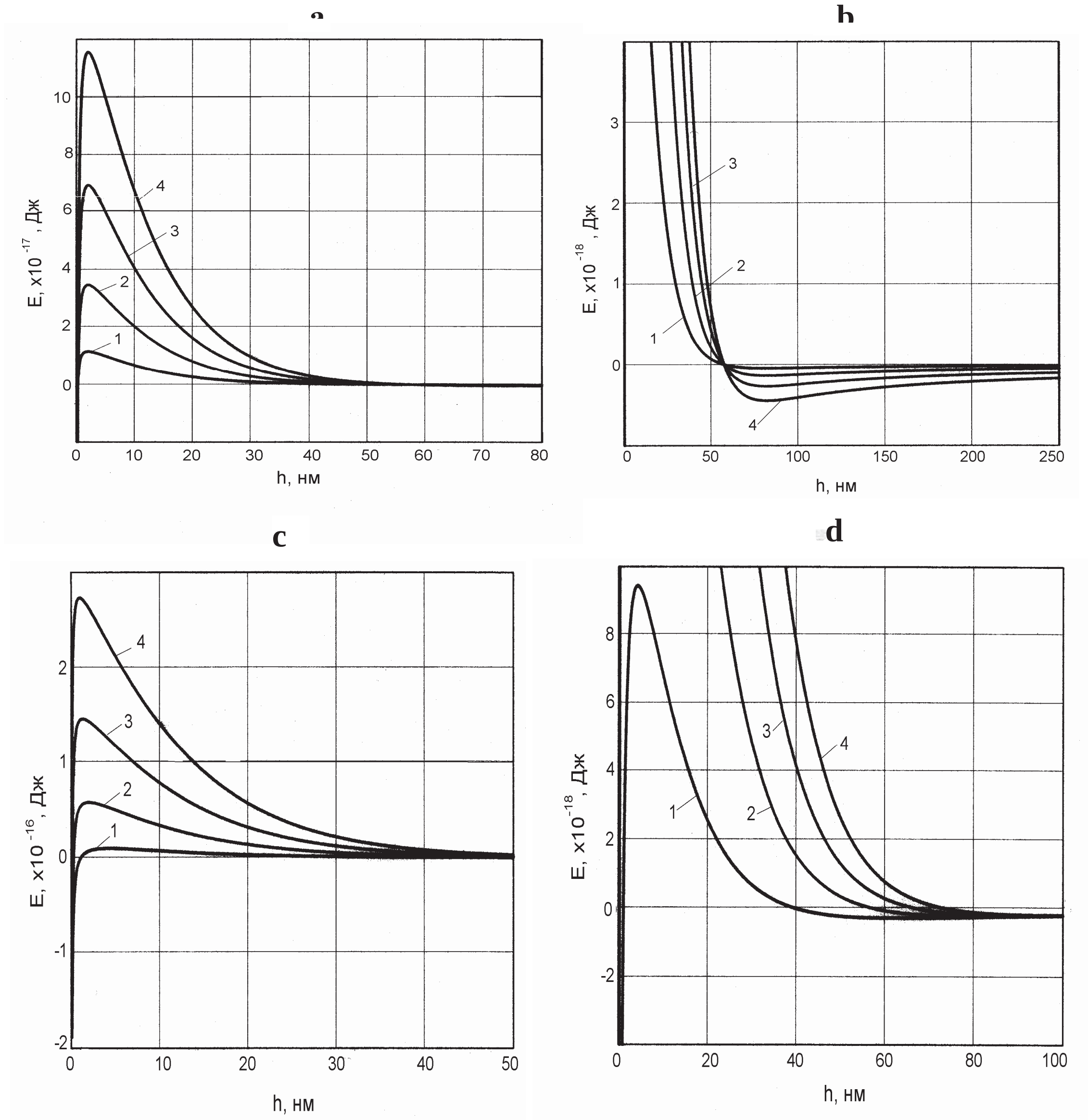

Fig. 3 Analytic dependences $E_c(h)$:
a, b – at the mineral particle size: 1 – 1 μm; 2 – 3 μm; 3 – 6 μm; 4 – 10 μm; – general survey scale of the curves; b – detailed against the axis E_c); c, d – at the variation of the mineral particle surface potential within 50-200 mV: 1 – 50 mV; 2 – 100 mV; 3 – 150 mV; 4 – 200 mV
(c – general survey scale of the curves; d – detailed against the axis E_c)

the “second potential well” grow with a larger size of mineral grains. The first of the indicated phenomena, the increased energy barrier of repulsion, leads to a higher aggregative stability as the barrier prevents the particles from getting into and irreversible coagulation in the “first potential well”. The second phenomenon, the deepening of the “second potential well”, contributes to a higher stability of the thyxotropic structure of mineral slurry. The deeper this potential well, the higher the interparticle interaction energy in the reverse coagulation structures and the higher the stability of mineral particle slurry.

The indicated regularities are similar to those we established for coal particles i.e. they are of universal nature for the entire HLCWS soild phase. In practice, however, the repulsion barrier height of mineral particles is much smaller than that of HLCWS coal grains (from several times to 10 times) due to a smaller size of mineral grains and a lower Hamaker constant which reflects physical and chemical properties of the solid surface of substance. This governs their greater tendency to irreversible coagulation at the first energy minimum.

Figs. 3 c, d show the curves $E_c(h)$ for the total potential of the mineral particle surface changing within 50-200 mV мВ at the grain size $d_з$ = 5 μm and the Hamaker constant $A_r = 1 \cdot 10^{-19}$ J.

An analysis of the curves obtained indicates that an increase in the potential of the mineral surface results in the energy barrier of repulsion which keeps growing. This barrier appears at $\varphi \approx 50$ mV, similarly to coal grains. At $\varphi < 50$ mV mineral slurry is aggregatively unstable. Under the influence of dispersive Van der Waals interactions, its grains irreversibly coagulate with each other and mineral slurry laminates.

At $\varphi > 50$ mV, similarly to the pair "coal grain – coal grain", there are two typical effects observed for the pair "mineral grain – mineral grain" under consideration. Firstly, the repulsion barrier height significantly grows, which correspondingly increases the aggregative stability of mineral slurry. Secondly, the coordinate of the second power well h_{m2} shifts to the right. This results in a larger distance between mineral particles which get retained in the second potential well of the thyxotropic structure. As a consequence, the water content of slurry for the mineral component with a relatively large surface potential gets increased (and correspondingly its solid phase concentration is reduced).

The data obtained demonstrate that with the variation of the total surface potential of mineral and coal particles the behavior patterns of the curves $E_c(h)$ are similar. For the assumed actual conditions of HLCWS the barrier height of repulsion in case of mineral particles is reduced roughly by an order of magnitude versus coal grains, with the surface potential values equal. In other words, it is another confirmation of the fact that mineral slurry tends more to irreversible coagulation at the first energy minimum.

It is also useful to analyze the influence of the nature of the particles comprised by mineral slurry on its energy state. The difference in the material composition of the slurry mineral component is evaluated in DLVO theory with the help of the Hamaker constant.

As known [4], the stronger the mineral phase interacts with water, the lower the Hamaker constant A_r is, i.e. the attracting forces between slurry particles get weaker. The increasing value of the constant Ar corresponds to the growing hydrophobial properties of the mineral surface. The analytical curves $E_c(h)$, which we obtained, with A_r changing over the range of $(0.2\text{-}2.0) \cdot 10^{-19}$ J, and at $d_з$ = 5 μm, φ = 100 mV, confirm this thesis and show that the growing hydrophobous properties of mineral particles result in some decrease of the barrier height of repulsion and hence in lower aggregative stability of mineral slurry.

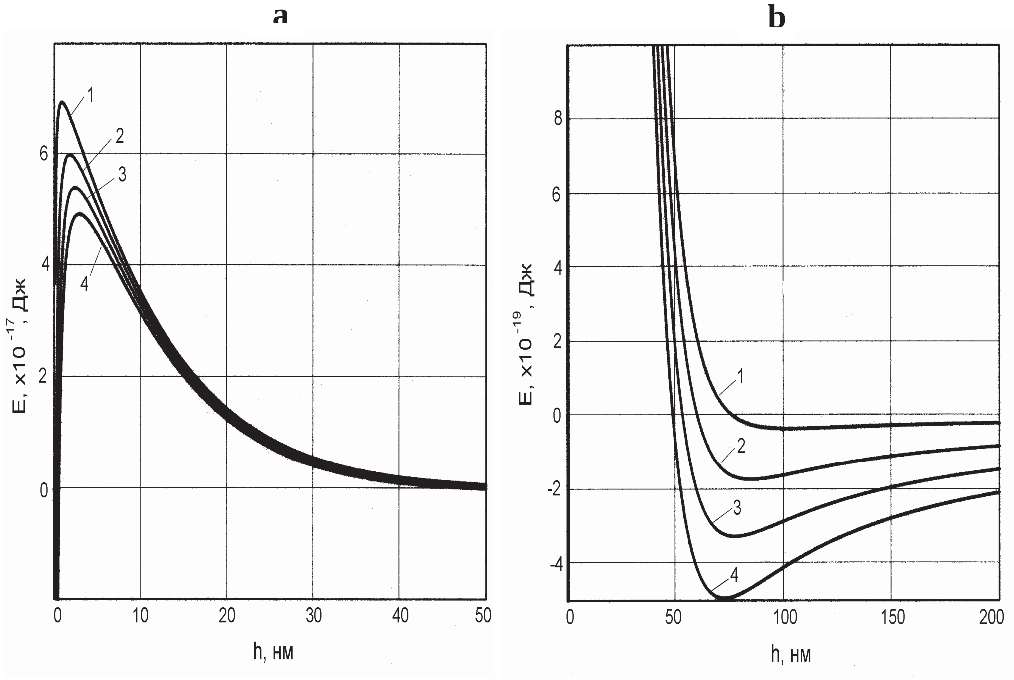

Fig. 4. Analytic dependences $E_c(h)$ for mineral particles, with the Hamaker constant changing: 1–A_r = 0.2 ·10^{-19} J; 2–A_r =0.8·10^{-19}J; 3–A_r = 1.4·10^{-19} J; 4 – A_r = 2.0 ·10^{-19} J (a – general survey scale of the curves; b – detailed against the axis E_c).

As seen in Fig. 4, the increase in the Hamaker constant is accompanied by the deepening of the second energy minimum i.e. a higher probability and strength of slurry mineral particle retention at the second potential minimum.

Thus, two opposite tendencies of the influence of the mineral matter nature on slurry characteristics are observed. On the one part, with the increasing A_r the aggregative stability of slurry is reduced to irreversible coagulation. On the other part, thixotropic properties of mineral slurry get stronger (formation of a spatial “grid” of mineral grains retained in the second potential well).

It should be noted that the second tendency dominates over the first one, that is under similar conditions the second potential well deepens approximately 10 times whereas the height of the repulsion potential barrier is reduced by only 1.5 times.

The essential difference observed in the behavior of mineral grains of different nature in the second potential well is confirmed by data of empiric research [10]. In other words, the material composition of the HLCWS mineral component is a separate factor influencing thixotropic characteristics of coal-water slurry.

Conclusions.

1. Application of DLVO theory for analyzing the energy state of the solid phase of highly-loaded coal-water slurries is a promising instrument for inves-

tigating this object and may underpin the HLCWS theory. Specifically, use of DLVO theory allows to explain the nature of phenomena that take place with changes to the size and surface potential of coal and mineral particles as well as their surface hydrophilous-hydrophobous balance.

2. The performed analysis of the energy curves $E_c(h)$ which we obtained shows that at relatively low surface potentials of coal particles ($\varphi < 50$ mV) coal-water slurry is aggregatively unstable.

3. A higher particle potential of coarsely dispersed colloid systems in the area $\varphi > 50$ mV results in a better aggregative stability of coal-water slurries. However, in case of coal with the surface potential $\varphi > 50$ mV the distance between coal particles retained in the "second potential well" of the energy curves $E_c(h)$, is observed to increase, which leads to a larger water content of HLCWS.

4. The growing hydrophobic properties of the coal surface somewhat reduce the HLCWS aggregative stability.

In case of particle retention at the first potential minimum the strength of their bonding prevents laminar flow of slurry from destroying these structures throughout the investigated range of the size and surface potential of the HLCWS solid phase. This results in the "aging" effect of HLCWS and the necessity to recover its previous tubular mixing characteristics, for example in pumps.

A promising line of follow-up study is impact assessment of a mechanical and chemical destruction of the solid phase as well as opening of pores on HLCWS properties.

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SAVYK V.M., Ph.D, Assistant Prof., MOLCHANOV P.O., Ph.D, Assistant Prof., Poltava National Technical University named in honour of Yuriy Kondratyuk

THE RAISING OF EFFICIENCE OF CIRCULATED SYSTEM IN DRILLING SET DURING DRILLING WITH WELL WASHING BY THE FOAM

There has been analyzed the existing schemes of strapping of circulated system of drilling set during drilling with well washing by the foam and argued the necessity of its efficient raising; there has been chosen the scheme of strapping of circulated system during drilling with well washing by the foam for the possibility of the most rational usage of existing foamgenerating equipment.

В статті проаналізовані існуючі схеми обв'язки циркуляційної системи бурової установки при бурінні з промиванням свердловини піною та обґрунтована необхідність підвищення їх ефективності; для можливості найбільш раціонального використання існуючого піногенеруючого устаткування передбачена схема обв'язки циркуляційної системи при бурінні з промиванням свердловини піною.

В статье проанализированы существующие схемы обвязки циркуляционной системы буровой установки при бурении с промывкой скважины пеной и обоснована необходимость повышения их эффективности; для возможности наиболее рационального использования существующего пеногенерующего оборудования предусмотрена схема обвязки циркуляционной системы при бурении с промывкой скважины пеной.

The choice of issue and its connection with vital scientific and practical tasks. The foam is highly plastic and elastic system that differs from other drilling solution. Foam systems have relatively permanent character only in the process of circulation in the well with set parameters of mode and known circumstances. After circulative stop (the stop of pump and compressor) the system becomes inconstant, elastic features can be shown and the division of phases can carry out, hence the pressure of foam in the output decreases after some period of time. That's why we have produced the foamgenerating device for creation of high-quality small-dispersed foam that treats the requirements which could concern its during washing of oil and gas wells [1–4].