Study of the Change in the Coal-and-Liquid-and-Gas Interfacial Angle

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Abstract. The use of surfactants has a significant impact on the safety of mining operations in order to prevent dynamic processes, prevent dust. The interfacial angle is the main indicator characterizing the interfacial interactions for heterogeneous multicomponent solid bodies, coal and solutions. The problem of development of modern methods for determining the interfacial angle at the coal-water-gas boundary is considered. The results of the research study of the change in the coal-liquid-gas interfacial angle are presented. The influence of various coal properties and characteristics on the interfacial angle value is shown. The influence of the interfacial angle on wetting and filtration processes, the features of the experimental methods for the interfacial angle determination are shown. A model of the coal surface consisting of four main components is proposed. The main attention is paid to the moisture content of coal and capillaries as the main factors determining the properties of coal. An analytical method for determining the interfacial angle of coal-water-gas is proposed.

1 Introduction

Surfactant water solution technologies are increasingly being used in modern mining industry. The main areas of use of surfactant solutions are: improving the mine safety, increasing the recovery efficiencies. In particular, the use of surfactants for the coal massif pre-wetting makes it possible to reduce gas emissions into mine workings by 65-75% and also the dustiness of the atmosphere to 80%; reduce the coal bed gas-dynamic activity; align strike and formation strength volumes using the coal massif pre-wetting technology [1-4]. In the process of filtration and surfactant solution wetting, the coal massif stress-strain properties change, which affects the safety of mining coal beds that are prone to sudden outbursts, liable to rock-bumps, etc. [4].

One of the topical problems of increasing the efficiency of the use of surfactants is the development of surfactants, which allows solving the technological problems universally [5], [6]. In this connection, at the present stage, a detailed study of the coal-liquid-gas interfacial interaction is urgent.

The purpose and objectives of these studies are:

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1) study of the interfacial interaction in the coal-liquid-gas system;
2) modeling of the interfacial interaction in the coal-liquid-gas system;
3) development of the methods for the coal-liquid-gas interfacial angle determination.

2 Research materials and methods

Coals of various grades, ranks, physical and chemical properties, moisture content, various rocks with different structural features, porosity, strength characteristics, as well as distilled water, various surfactants were used for experimental studies. The most common in the mining industry "Neolas", "Elfor", etc., were used as surfactants.

From the common knowledge it follows that interfacial angle Θ [7-9] is one of the main indicators of the coal-surfactant solution-gas or the solid-surfactant solution-air interfacial interactions. The following factors influence the choice of this variable as the main for the studies [4], [5]:
1) the structure of the study solid: porosity, coal heterogeneity;
2) physical and chemical properties of the study liquid;
3) the goals and objectives of the process under consideration.

A generalized characteristic of the action of Laplace forces when wetting the surface, which determines the process direction, is wettability, defined by the formula $k = \sigma \cos \Theta$, where σ – is surface tension factor. Surface tension factor σ shows only the energy properties of a given liquid, the ability of a liquid to interact with other substances. This factor is of significant importance for these studies. From the point of view of physical and chemical knowledge, the interfacial angle Θ is determined by the relation between the acting surface forces at the interface between the phases, characterizes the ratio of the acting surface energies at the interface of the interacting phases. In this case, it is the most informative characteristic of interfacial interactions. The interfacial angle Θ is the main indicator characterizing the interfacial interactions, the efficiency of many processes, both in mining and in other industries. The angle Θ variations being studied; the possible conditions for the efficient process control are determined [6-10].

Taking into account that coal is a structurally complex capillary-porous solid body that is heterogeneous both in structure, and in chemical composition and properties. Therefore, complex generalized macroscopic properties will more accurately characterize the main properties of this research object in interactions with other substances, surfactant solution, gas.

There are many experimental methods and Θ determination methods. The most famous method is sessile drop method, in which the angle Θ is determined from the angle between the tangent drawn to the wetting liquid surface and the wettable solid surface through the point of contact of the three phases.

We note that the methods under consideration, and in particular sessile drop method, are oriented at angles in the range from 30 to 150 degrees, obtained at the interface between homogeneous solids and liquids. Within these range, the results have the smallest measurement error, which is 2-4% for the relative error. For angles less than 30 degrees, the relative error increases significantly, reaching 20%. Therefore, it is urgent to develop measurement methods for interfacial angles of less than five degrees, oriented to specific media and their interfacial interactions, in particular coal and surfactant solutions.

Using modern technical achievements, this method is also being improved, allowing on the one hand automating the measurement process and simultaneously improving the accuracy of measurements, on the other hand [7], [9],.

Based on this method and the application of IT technologies, we developed a method for measuring the coal-liquid-gas interfacial angle. To carry out the research, an optical bench with holders was used, on which the main elements were fixed: a camera, an object table with the study polished section of coal or other material. A drop of the study liquid was deposited on the surface of the coal polished section and photographed. The image was transferred to a computer where, using the developed technique, processing of measurement results was carried out with the help of graphic and analytical programs, angle Θ was determined. The developed research technique made it possible to increase the accuracy of determining the angle Θ for small values.

When determining angle Θ the following formulas were used.

1. If $\Theta \le 90°$, the following formula is used to calculate the angle Θ:

$$\sin\Theta = \frac{r}{R}, \quad (1)$$

where *r*, *R* – radius of the base and the radius of the spherical segment of a drop (fig. 1).

2. If $\Theta > 90°$, the following formula is used:

$$\Theta = \arccos\frac{r}{R} + 90^{\circ} \text{ или } \cos(\Theta - 90) = \frac{r}{R} \quad (2)$$

3. For small angles $0° < \Theta < 15°$ the following Θ angle determination method is used. Knowing the mass of the drop placed on the surface of the polished section, the height *h* of the spherical segment is found from equation:

$$m_{\kappa} = \rho V = \rho\frac{1}{6}\pi h(h^2 + 3r^2),$$

where m_{κ}, *V* – drop mass and volume.

Then, angle Θ is found by formula

$$\mathrm{tg}\Theta = \frac{2hr}{r^2 - h^2} \text{ или } \sin\Theta = \frac{2hr}{r^2 + h^2},$$

where it is taken into account that for small values *R*>>*r*, *r*>>*h* of the angle Θ, it is advisable to measure the radius of the base of the spherical layer *r*.

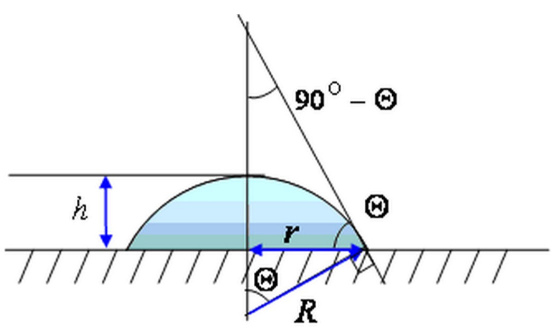

Fig.1. The angle Θ detection scheme.

3 Results

According to the results of the research, it is shown that due to the high anisotropy and coal heterogeneity, the results of the angle Θ measurements will impact on the angle Θ determination accuracy in the experiment. The method of the surface (polished section) preparation for research, the roughness resulted from the coal surface treatment and the polished section preparation, the experimental conditions, and the surface cleanliness are of considerable importance for the results of the measurements. As a result, a significant change in the angle Θ, a hysteresis of the angle Θ, which depends primarily on microcapillary filtration in the near-surface layer at the point of direct contact between the coal and the liquid drop and the roughness of the polished section, is observed.

The surface of coal in terms of chemical composition varies significantly from one grade to another. In fact, each coal seam is unique in its physical and chemical properties. On the other hand, an increase in the porosity of coal in comparison with ordinary solids results in a significant increase in the effect of surface phenomena and properties on interfacial interactions [10].

In addition to the above factors, the coal-liquid-gas interfacial angle is significantly influenced by coal structure, degree of coal disturbance as a consequence of geophysical or production processes. Coal in its properties is a preferred direction anisotropic substance. According to the results of the measurements of the coal polished section angle Θ obtained parallel to bedding with the minimal destruction and the degree of machine dressing, the angle Θ takes values in a smaller range from 30 to 50 degrees. And, on the contrary, for highly disturbed coal, where the structure is significantly disturbed, the angle Θ assumes values greater than 120 degrees, especially for K and KZ grade coal of outburst-prone coal seams, which is also related to structural, physical and chemical features of the properties of these coals. An essential factor here is a higher specific pore surface area of outburst-prone seam coal, and, consequently, an increase in the effect of the hydrophobic part of coal on the final value of the angle Θ. On the other hand, there is the disturbance of the macromolecular structure of the coal substance leading to the formation of additional hydrophobic centers at the interface.

As a result of the studies carried out using the developed method, the time dependence of the change in the angle Θ and the time dependence of the rate in the change in angle Θ at the solid-liquid interface were obtained. Some of these dependencies are shown in fig. 2. The results of the studies show that a significant change in the angle Θ over time is characteristic for high porosity coals and when interacting with an optimum surfactant solution, with a surfactant concentration at which the filtration rate of solution is maximal. This indicates the activation of interfacial interactions and microfiltration of liquid in the near-surface layer of coal as a capillary-porous body. It is advisable to use methods that do not disturb the coal structure integrity during measurements or experiments, simultaneously taking into account both the coal wettability and filterability [4], [5].

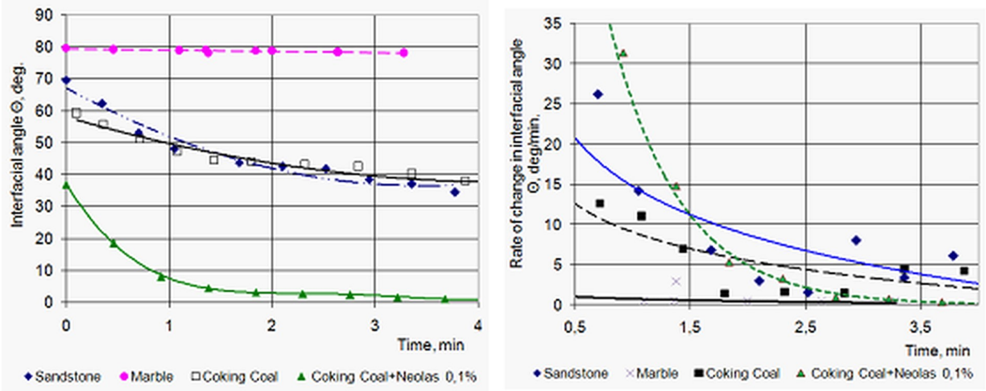

Fig. 2. Time dependence of the angle Θ and the rate of change in the angle Θ.

4 Discussion

Based on the experimental data analysis, we proposed an analytical method for estimating the angle Θ at the coal-water-gas interface from the ratio of the main structural components in the coal. The value of the interfacial angle depends on the physical and chemical nature of the interacting phases, the type of intermolecular interactions, the structure, the dispersion of impurities, and so on. According to [7], for a heterogeneous solid body surface, the angle Θ can be represented by the sum:

$$\cos\Theta = p_1\cos\Theta_1 + p_2\cos\Theta_2 + ... + p_n\cos\Theta_n , \quad (1)$$

where $p_1, p_2,..., p_n$ – relative fractions of the surface of solid components;

$\Theta_1, \Theta_2,..., \Theta_n$ – interfacial angle for every surface component.

The supplementary condition for the equation (1) is

$$p_1 + p_2 + ... + p_n = 1 \quad (2)$$

Based on the results of experiments and theoretical knowledge, four main components having a significant effect on the final value of the angle Θ can be detected:

1) humidity;
2) rank;
3) dirt content, ash content;
4) porosity.

Using the results of experimental studies, surface modeling based on formulas (1) and (2), the angle Θ at the coal-water-gas interface will be determined by the formula:

$$\cos\Theta = \sqrt[3]{(A_v - W)^2}\cos\Theta_A + k_W\sqrt[3]{W^2}\cos\Theta_W + \sqrt[3]{(P-W)^2}\cos\Theta_P + \\ + \left[1 - \sqrt[3]{(A_v - W)^2} - k_W\sqrt[3]{W^2} - \sqrt[3]{(P-W)^2}\right]\cos\Theta_M \quad (3)$$

where A_v – volume ratio of mineral matter in coal; W – volume ratio of water in coal; P – porosity; Θ_A – the interfacial angle for the mineral component of coal – 20 – 30°; Θ_W – the same at the liquid-liquid system interface, Θ_W =0°; Θ_P – the interfacial angle of pores – 60 – 80°; Θ_M – the interfacial angle of organic part of coal; k_W – semi-empirical ratio, associated with water distribution in pore volume and spread layer at the coal-water-gas interface, equal to 6 – 7.

The angle Θ_M is detected similarly (1) by formula:

$$\cos\Theta_M = \frac{p_C}{p_C + p_O}\cos\Theta_C + \frac{p_O}{p_C + p_O}\cos\Theta_O , \quad (4)$$

where p_C – volume ratio of carbon in organic part of coal; p_O – volume ratio of oxygen in organic part of coal; Θ_C – the interfacial angle for carbon compounds like graphite; Θ_O – the interfacial angle for oxygenated surfaces.

The research results show that the change in the carbon content in the organic part of coal over the entire coal ranking range changes its hydrophilic properties by 6 – 7°, i.e. the effect of changes in the organic part of coal on the coal wetting ability is insignificant. The similar results are given by a change in the ash content of coal over the entire range from 3 to 16%.

It should be noted that the greatest influence on the hydrophilic properties of coal is caused by a change in its moisture content. From the above dependences it follows that the physical and chemical structure of coal determines its wetting ability degree, determines the value of natural moisture. Thus, natural moisture and air dried moisture determine the hydrophilic properties of coal.

5 Conclusions

The analysis of the conducted experimental studies and the interaction process modeling allow drawing the following conclusions:

1. The main characteristic of the coal-liquid-gas interfacial interactions is the interfacial angle;
2. Molecular structure of coal matter and its physical properties, moisture, porosity will determine the molecular structure of the most effective surfactant for coal wetting;
3. Hysteresis of the interfacial angle is observed as a result of the media interfacial interactions that take place for some time.

According to the research results it was shown that the water content (natural moisture) in coal is the main factor determining the coal-water-gas interfacial angle value, and also the important basic informative index of hydrophilic properties of coal, is a consequence of other initial factors: petrography, rank, ash content, and porosity.

The obtained results can be used in the design of technologies for reducing gas emission, dust forming, coal bed pre-wetting used to control a coal massif condition using surfactant solutions. The ratio of the hydrophilic and hydrophobic components of the coal surface will determine the surfactant structure, its properties for the effective surfactant solution wetting process.

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