Investigations of imbibition and wetting properties of aqueous solutions of sodium dodecyl sulfate on porous beds of hydrophilic and hydrophobic materials

ANDRZEJ MIZERSKI, SŁAWOMIR NEFFE[1]

The Main School of Fire Service, Warsaw, Poland, a_mizerski@poczta.onet.pl
[1]Military University of Technology, Faculty of Advanced Technologies and Chemistry, Warsaw, Poland, sneffe@wat.edu.pl

Abstract. The kinetic of imbibition of porous beds of different materials, with water solutions of sodium dodecylsulfate was investigated. The following materials were used: four kinds of active carbons: Norit R 08 EXTRA, Norit ROX 08, DTO and Merck; three kinds of mineral coals: hard coal, brown coal and peat; two kinds of graphite: natural Ceylon graphite, synthetic Acheson graphite and powdered sulfur. The kinetics of imbibition was tested using the capillary rise method, with the flow of liquid in the upward direction. The results are presented in the form of graphs showing changes of the saturation versus the time of imbuing the layer. Also, the influence of adsorption of sodium dodecyl sulfate from the solutions on the kinetics of wetting was investigated. The results showed that mineral coals, graphite and sulfur did not imbibed water easily, while active carbons and synthetic graphite were hydrophilic, though in different degrees, and had high imbibition coefficient. These findings were discussed in the aspect of their usefulness in the fire fighting technology.
Keywords: surface effects on porous materials, surface active substances, fire fighting technologies

1. Introduction

What we know about the influence of surfactants (surface active substances) on the process of wetting and imbibition of porous materials' layers is not always appropriately applied in firefighting practice. Knowing and understanding the wetting mechanisms allows us not only to decide whether surfactants are appli-

cable in a given situation, but also to determine the direction of research for new fire-fighting foaming and wetting agents.

Increasing the effectiveness of fire-fighting action and thus shortening the extinguishing time results in many advantages, such as:

— decreased amount of losses caused by the fire,
— decreased consumption of water,
— decreased emission of harmful substances produced during the fire,
— decreased amount of harmful substances — products of partial combustion and pyrolysis (thermal decomposition), which are removed with water from the fire zone and get into the environment,
— more safe and comfortable working conditions for fire-fighters.

Fighting the fires of many porous materials and of loose materials' layers is particularly difficult. In such fires, flameless combustion deep in the material's structure can takes place, hence, in order to extinguish them, the inside of the material must be cooled. However, fine-porous structure of the layer together with hydrophobic character of the surface can make water absorption difficult. In many cases fire-fighting effectiveness can be increased by adding surfactants to the water. Surfactants are usually synthetic foaming agents, applied in lower concentrations than would be needed to generate foam. There is a recent tendency to use the so called class A foams, with low expansion ratio, made from water solutions of surfactants with high surface activity, so that the surfactant concentration in water can be very low. There are situations, however, in which using surfactants are ineffective, such as subsurface fires of hydrophobic (low wettability) materials, for example peat lands or hard and brown coal dumps. There are also cases in which surfactant addition slows down the process of wetting.

Explanation this questions requires defining the wettability of several materials with distinct hydrophobic and hydrophilic properties, as well as, determining the role of surfactants adsorption from water solutions on the surface of studied materials in the whole process.

The aim of the paper presented here is to investigate the surfactants' effect on the wetting and imbibition rate of hydrophilic, as well as hydrophobic materials' layers and also to assess whether adding surfactants to water is applicable when fighting subsurface fires of fine-porous layers of different carbonaceous materials.

2. Theory

The average linear rate of flow of liquid with the absolute viscosity η through a cylindrical capillary tube with the radius r, on a distance with the length l, is described by the Poiseuille's equation [1, 2].

$$\frac{dl}{d\tau} = \frac{r^2 \cdot \Delta P}{8\eta \cdot l}. \tag{1}$$

When the flow is free, unconstrained, the pressure ΔP is an algebraic sum of the capillary pressure, described by the Laplace's equation, and the hydrostatic pressure of liquid column in the capillary:

$$\Delta P = \frac{2\sigma \cdot \cos\theta}{r} \mp \rho \cdot g \cdot l \sin\alpha, \tag{2}$$

where: σ is surface tension of the liquid, θ — contact angle of wetting the capillary surface with the liquid, ρ — the liquid's density, g — gravity acceleration, α — inclination angle of the capillary.

The plus or minus sign between the two pressures depends on the direction of the liquid's flow and on the value of the contact angle. For small radii of the capillaries, the impact of hydrostatic pressure can be omitted, and thus the equation (1) will take the form of:

$$\frac{dl}{d\tau} = \frac{r \cdot \sigma \cdot \cos\theta}{4\eta \cdot l} \quad \Rightarrow \quad \int_0^l \frac{4\eta \cdot l}{r \cdot \sigma \cdot \cos\theta} dl = \int_0^\tau d\tau \tag{3}$$

and after integration:

$$l = \sqrt{\frac{r \cdot \sigma \cdot \cos\theta \cdot \tau}{2\eta}}. \tag{4}$$

In case of unary liquids, the surface tension, contact angle and viscosity remain constant during the flow, and the length of the wetted capillary can be expressed by the formula:

$$l = K\sqrt{\tau}. \tag{5}$$

This equation (5) is correct for material layers fulfilling the assumptions of the cylindrical capillary model [3, 4]. For actual layers, the constant K has the form of [4]:

$$K = \sqrt{\frac{r_z \cdot \sigma \cdot \cos\theta}{2k^2 \cdot \eta}}, \tag{6}$$

where: k is a factor that takes into account the sinuosity of capillaries, and r_z — the capillaries' effective radius, defined as follows [4]:

$$r_z = \frac{2\varepsilon}{S_k \cdot \rho_s \left(1-\varepsilon\right)}, \tag{7}$$

where: ε — porosity of the layer, ρ_s — density of the solid material [g/cm^3], S_k — kinetic specific surface per unit mass.

The formula (5) has a linear character for unary liquids. In case of a surfactant solution flow, the surface tension and contact angle change due to adsorption of active substance on the capillary's walls. The linear dependence is preserved when during the flow there remains a constant quantity $\sigma \cdot \cos\theta$, called the wetting tension [5].

3. Experimental

The wetting kinetics of 10 kinds of powdered and granulated materials layers — 5 hydrophilic and 5 hydrophobic — have been tested. The term *hydrophobic materials* refers to materials whose layers have not imbibed water due to the impact of capillary forces only. From the Laplace's equation (2) a conclusion can be drawn that in such cases the water wetting contact angle is larger than or equal to 90°, which is a commonly used criterion pointing to the hydrophobic character of a given material. The hydrophobic materials tested were: brown coal, hard coal, peat, natural Ceylon graphite and powdered sulfur, and the hydrophilic materials: synthetic Acheson graphite and four kinds of active coals — Norit R 08 EXTRA, Norit ROX 08, DTO and Merck. These materials are described in detail later in this paper.

The surface active substance (surfactant) applied in the tests was sodium dodecyl sulfate (SDS), ultrapure (> 99%) prod. CARL ROTH GmbH & Co. It is slightly soluble in water an its aqueous solutions became cloudy after some time, hence, for the purpose of the tests, a liquid concentrate was made, containing: 20% sodium dodecylsulfate, 25% butyl carbitol (diethylene glycol monobutyl ether, pure prod. FLUKA) and 55% distilled water. Butyl carbitol is primarily used as a solvent in extinguishing foaming concentrates.

3. 1.   Properties of tested materials

The powdered materials tested have been characterized by defining the size analysis, density ρ_s, kinetic (S_k) and adsorptive (S_a) specific surface area, and moisture content W (tab. 1).

Grain size analysis was carried out using an Infrared Particle Size Analyzer (IPSA), made by KµK Company, Poland. To define density (ρ_s), the materials' volume was determined with the pycnometric method, using extra pure ethanol. This density may differ from the real density if there are closed pores inside the

material, but it can be used for calculating open porosity, which in turn is used in the quantitative description of the kinetics of layers' saturation.

Kinetic specific surface (S_k) was determined with a Blaine's surface meter, by measuring the time in which a defined volume of air flows through a layer of compressed material, for which the volume and section area is given. Adsorptive specific surface (S_a) was tested with a GEMINI 2360 V2.01 apparatus, made by Micromeritics, USA. The measurement consists in determining a low temperature isotherm of nitrogen adsorption, using the BET method. Moisture content was determined by measuring the mass loss of the sample in drier-scales, at a temperature of 106°C.

Granulated active coal DTO consisted of spherical grains 0.2-1.5 mm in size, with the majority varying from 0.5 to 1.0 mm. Norit R 08 EXTRA and Norit ROX 08 coals had the form of cylindrical granules, and their average dimensions: height h and diameter d, as given by the producer, were as follows: Norit R 08 EXTRA: $h = 1.37$ mm, $d = 0.79$ mm; Norit ROX 08: $h = 2.26$ mm, $d = 0.81$ mm. Due to the large size of the grains, resistance of air flow through their layers was slight and measurement using the Blaine's surface meter was not possible. Kinetic specific surfaces of these active coals were therefore calculated on the basis of the average outer dimensions of the granules.

TABLE 1

Physical parameters of powdered or granulated materials tested

Material		Part of fraction [mm] [%]			ρ [g/cm^3]	S_a [m^2/g]	S_k [cm^2/g]	W [%]
		< 0,05	< 0,1	< 0,2				
Active carbon	Norit R 08 EXTRA	granulated			1,93	1185	160	1,6
	Norit ROX 08	granulated			1,58	819	149	2,7
	DTO	granulated			1,85	810	1740	12,8
	Merck	42	80	100	1,59	1116	8650	14,4
Synthetic Acheson graphite		35	88	100	2,26	8,8	4400	0,6
Natural Ceylon graphite		33	87	99	1,72	4,4	5850	0,6
Peat		13	51	93	1,44	1,1	4780	8,9
Brown coal		30	77	99	1,36	1,7	3810	8,2
Hard coal		56	98	100	1,36	2,9	4430	3,5
Sulphur		18	57	79	1,90	0,2	1450	0,1

ρ_s — density, (S_k) — kinetic specific surface, (S_a) — adsorptive specific surface, W — moisture content

The active substance content in the SDS concentrate used in the tests, determined using the method of two-phase titration [6], was 0.64 M/dm^3. The SDS water solutions

did not become cloudy, hence the measurement was not disturbed by the formation of a two-phase system (suspended matter) in the solution. Changes of surface tension with the SDS concentration in distilled water are presented in Fig. 1.
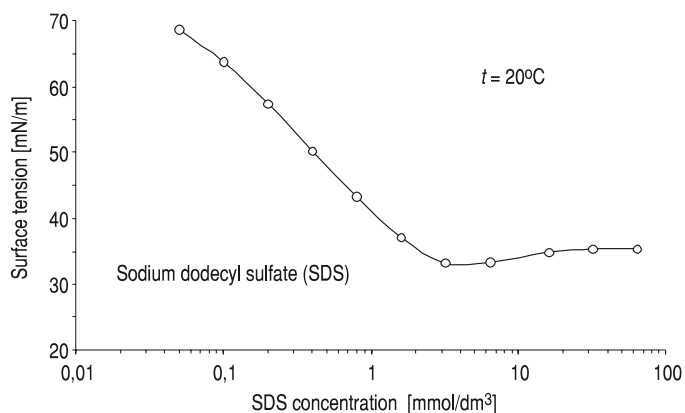

Fig. 1. Changes of surface tension with the SDS concentration in water solutions

The surface tension was measured with a DuNouy tensiometer (made by CSC Scientific Company, Inc, USA), using the ring method. The course of the surface tension isotherm is characteristic of anionic surfactants [1]. The slight minimum is probably related to the presence of small amount of impurities with greater surface activity, e.g. dodecyl alcohol. The critical micelle concentration (CMC) is approx. 0.5%, which corresponds to the concentration of 3.2 mM/dm^3. This value is lower than the CMC for sodium dodecyl sulfate that can be found in the literature, namely approximately 8 mM/dm^3 [7, 8]. This could be due to the presence of the organic solvent (diethylene glycol monobutyl ether).

3. 2.   Imbuing the layers

The wetting of layers was tested using the method of capillary rise in the upward direction, in the laboratory set presented in Fig. 2.

The layers were prepared in polyethylene tubes, 21 mm in diameter, with perforated bases, on which filter paper and a material sample weighed, with a precision of 0.001 g, were placed. The layer was exposed to vibration in standard conditions for 30 seconds. Next, the filter paper was put on top and the layer was compressed with a perforated piston to a defined volume, constant for each sample in the given series of measurements. The tube with the sample was hung on an electronic scales' pan, connected to a computer. The computer software allowed recording of the sample tube's mass at any time. A vessel 50 mm in diameter containing 50 cm^3 of liquid was lifted so as to achieve 2 mm immersion of the sample tube. At that moment
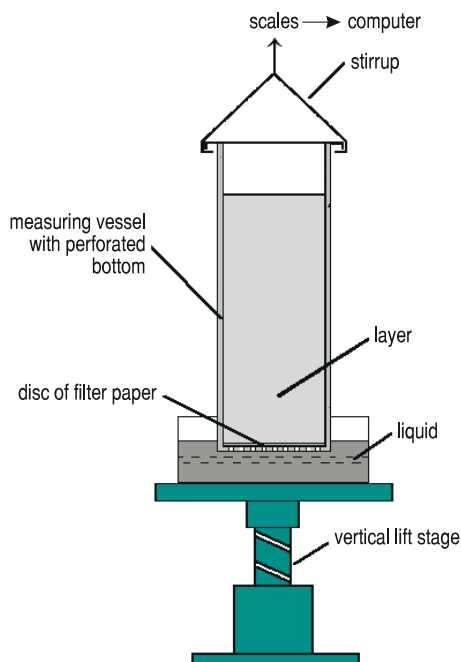
Fig. 2. Measurement set used for testing the kinetics of imbuing the layers

the scales were set to zero and the measurement cycle started, in which the sample's mass increase was recorded at given intervals of time. The cycles continued until no mass increase was noted in three subsequent measurements, or for 100 minutes in case of hydrophobic material samples. The mass changes were recorded in the form of a table and transformed to a graph as a kinetic relationships.

Several different powdered materials were tested, so the layers' volumes differed. The volume of each layer was selected in such a way that the time of the layer's imbibition of well wetting liquid was not shorter than 3 min. Parameters of the tested materials' layers are presented in Table 2.

TABLE 2

Parameters of the tested materials layers

	Material	m [g]	V [cm^3]	ε [–]	r_z [μm]
Active carbon	Norit R 08 EXTRA	1,00	2,5	0,79	243
	Norit ROX 08	1,00	2,6	0,75	255
	DTO	1,00	2,1	0,74	18
	Merck	1,50	2,7	0,65	2,7
Synthetic Acheson graphite		2,50	2,0	0,45	1,6

cont. table 2

Natural Ceylon graphite	1,50	2,0	0,56	2,5
Peat	1,00	2,0	0,65	5,4
Brown coal	1,50	2,5	0,56	4,9
Hard coal	1,50	2,0	0,45	2,7
Sulphur	2,00	3,0	0,65	13

m — mass of the material; V — volume of the layer; ε — porosity; r_z — effective radius of the pores

The layers' porosity ε was calculated using the formula:

$$\varepsilon = 1 - \frac{m}{\rho_s \cdot V}, \tag{8}$$

where: m — mass of the material [g]; ρ_s — density of the material [g/m^3]; V — volume of the layer [cm^3].

It is open porosity, not accounting for closed pores content. The pores' effective radius (r_z) was calculated using the formula (7).

The layers were subjected to capillary rise with water, ethanol (as the model liquid with excellent wettability — contact angle $\theta = 0$), and the solutions of sodium dodecyl sulfate in distilled water at 1, 2, 5, and 10% concentrations. The dependence $m = f(\tau)$, obtained from the measurement, was transformed into the function of the saturation ratio of the layer versus time. The saturation ratio (Φ) was defined as the ratio of the volume of the liquid imbibed by the layer to the total volume of the porous space, excluding closed pores:

$$\Phi = \frac{V_1}{\varepsilon \cdot V} = \frac{\Delta m}{\rho_1 \cdot \varepsilon \cdot V}, \tag{9}$$

where: V_1 — volume of the liquid [cm^3]; ε — porosity; V — volume of the layer [cm^3]; Δm — mass of the liquid (the layer's mass increase) [g]; ρ_1 — density of the liquid [g/cm^3].

3. 3. Adsorption of SDS from water solutions on the powdered materials tested

SDS adsorption on powdered materials was tested using the static method. It consisted in determining the difference of SDS concentration between the initial solution and the solution that was in the state of adsorption equilibrium with a solid adsorbent. In tightly closed vessels, 1 g of powdered material was covered with 25 cm^3 of various concentration SDS solutions. After adsorption equilibrium

was achieved, the concentration of the SDS solution above the solid adsorbent was measured. The adsorption value was calculated from the formula:

$$\Gamma = \frac{V_r\left(c_0 - c_1\right)}{m},$$ (10)

where: Γ — adsorption [mmole/g]; V_r — volume of the solution [dm^3]; c_0 — concentration of the initial solution [mM/dm^3]; m — mass of the adsorbent [g]; c_1 — concentration of the solution in the state of adsorption equilibrium [mmole/dm^3].

The concentration of the SDS solutions in the state of adsorption equilibrium was determined using the method of two-phase titration [6]. This method consisted in the titration of the anion-active substance (SDS) in a mixture consisting of the water phase, i.e. the solution tested, and the chloroform phase, with the standard solution of a cation-active surfactant, in the presence of a special indicator. The standard solution was benzyl-cetyl-dimethyl-ammonium chloride, analytically pure. The indicator consisted of a cationic colorant — dimidium bromide and an anionic one — disulfine blue.

4. Analysis of the test results

4. 1.   Kinetics of the layers' saturation

The measurement results of the imbuing time and the final saturation ratio are presented in Table 3. The most characteristic graphs $\Phi = f(\tau)$, showing the kinetics of the layers' saturation are presented in Figs. 3-4.

TABLE 3

Final test results of kinetics of imbuing the layers with water, ethanol and SDS solutions

Liquid		Ethanol		Water		SDS solutions							
						1%		2%		5%		10%	
Material		τ [s]	Φ [–]	τ [s]	Φ [–]	τ [s]	Φ [–]	τ [s]	Φ [–]	τ [s]	Φ [–]	τ [s]	Φ [–]
Hydrophilic	Norit R 08 EXTRA	30	0,99	100	0,65	100	0,58	100	0,56	100	0,48	100	0,71
	Norit ROX 08	25	0,96	8	0,94	25	0,92	40	0,95	100	0,90	100	0,84
	DTO	4,2	0,89	2,7	0,95	13	0,95	15	0,97	14	0,98	75	0,94
	Merck	4,5	0,91	3,5	0,99	4,5	0,94	6	0,99	8	0,93	5,5	0,92
	Synthetic Acheson graphite	8	1,00	6	0,94	8	0,91	14	0,89	15	0,89	17	0,90

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cont. table 3

Hydrophobic	Peat	2	0,81	100	0	100	0,04	100	0,07	100	0,20	100	0,39
	Brown coal	2	1,00	100	0	100	0,04	100	0,05	100	0,09	100	0,20
	Hard coal	4	0,98	100	0	100	0,57	100	0,71	9	0,98	5	0,98
	Natural Ceylon graphite	5	0,99	100	0	50	0,11	50	0,16	50	0,93	10	0,99
	Sulphur	1,1	0,92	100	0	42	1,00	10	0,92	3,5	0,92	0,9	0,92

τ — time of the layers imbibition; Φ — saturation ratio at τ
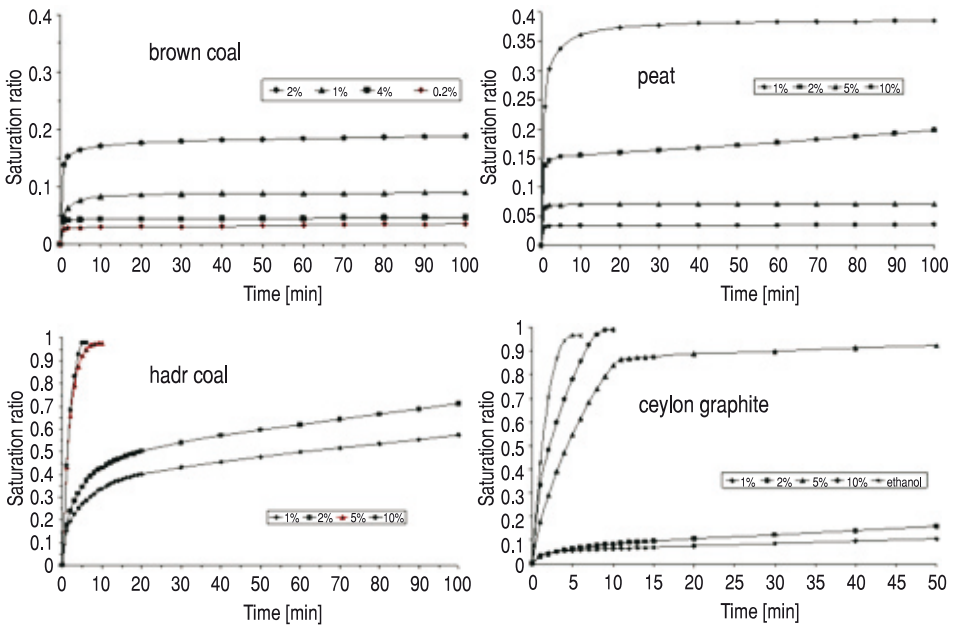
Fig. 3. Kinetics of imbuing of layers of hydrophobic materials with ethanol and the SDS concentrate of water solutions

Hydrophobic materials layers did not undergo the capillary rise, despite some slight overpressure (hydrostatic pressure of a 2 mm high column of water). Thus, a conclusion can be drawn that the contact angle of wetting these materials with water is bigger than 90°.

The experiments performed show that the process of imbuing hydrophobic materials layers with SDS solutions usually consists of two stages. In the first stage, the rate of imbuing (saturation) is high, and the corresponding segment of the curve is almost rectilinear. The second stage can be called the stage of wetting inhibition since the rate of imbuing is several times lower than in the first stage. Between the two stages, a transition period can be sometimes observed, lasting up
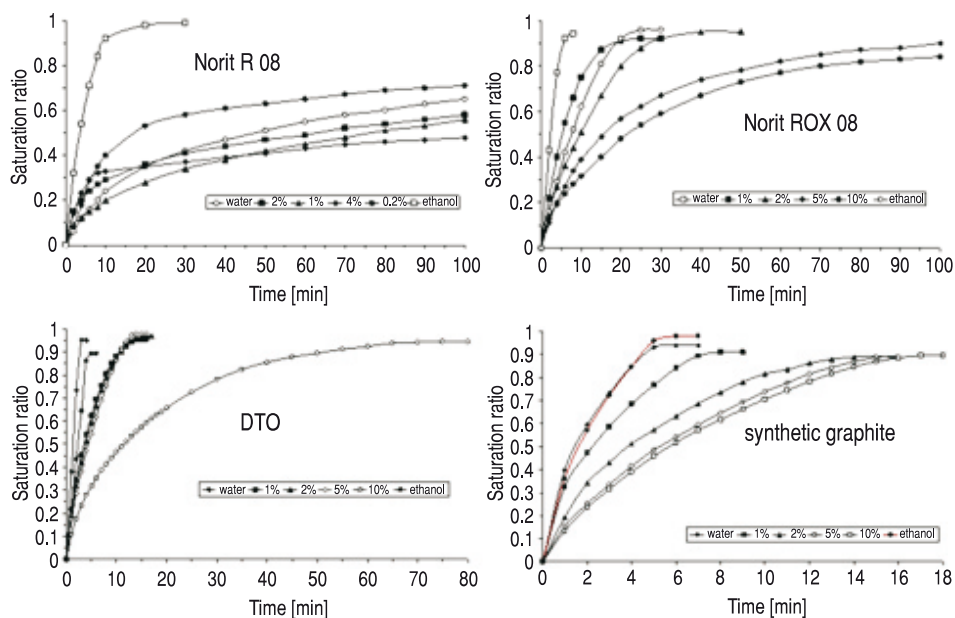
Fig. 4 Kinetics of imbuing the layers of hydrophilic materials with water, ethanol and the SDS concentrates of water solutions

to several minutes. In the second stage, the rate of imbuing is similar for all the SDS concentrations for which the inhibition of wetting is observed, which corresponds to the constant wetting tension ($\sigma \cdot \cos\theta$) in the area of the shifting meniscus of the liquid. Similar results have been obtained in the studies [4, 5, 9, 10, 11]. A layer's saturation ratio and the time after which the wetting is inhibited depend on the concentration of surfactant solution and the sort of material tested.

The saturation ratio in the moment of proceeding to the slow stage of imbuing the least wettable materials (brown coal, peat) is in direct proportion to the solution concentration, and the rate of imbuing in this slow stage is at low concentrations close to zero.

The tests performed have shown that hard coal and natural Ceylon graphite can be easier wetted with SDS solutions than peat and brown coal. In the case of the natural Ceylon graphite, inhibition of wetting can be still observed at 5% concentration, and the rate of imbuing in the slow stage is similar to that at 2% concentration and much lower than for hard coal at 1 and 2% concentrations.

Sulfur was the only hydrophobic material easily wettable with SDS water solutions. The rate of imbuing with 1% solution was low and did not change during the measurement. Higher concentration solutions penetrated sulfur layers at rates similar to those obtained for ethanol. Thus, it can be stated that the wettability of sulfur layers improved as a result of applying surface active substances.

All the hydrophobic materials were well wetted by ethanol, best of all peat and brown coal, which in turn were the least wettable by SDS solutions.

Adding sodium dodecyl sulfate to water caused a decrease in the rate of imbuing hydrophilic materials layers. Certain differences occurred only in the case of active coals Norit R 08 EXTRA and Merck. Besides, in the case of active coal DTO differences between 1, 2 and 5% concentrations were insignificant.

Among the active coals tested, Norit R 08 EXTRA was the least wettable with water. After 100 minutes the water saturation ratio was 0.65. It is a material composed of large granules; hence the capillary pressure in the inter-grain space is relatively low. It must be noted, though, that in the case of ethanol the saturation ratio of 0.99 was obtained after 30 minutes. As can be concluded from Table 3, the rate of imbuing the layers of Norit R 08 EXTRA active carbon was almost independent of the concentration of SDS solution.

The layers of Norit ROX 08 activated carbon imbibed water easily. This carbon granules are larger than those of Norit R 08 EXTRA carbon, for which complete saturation with water was not obtained. Thus, Norit R 08 EXTRA is less hydrophilic. The rate of imbuing Norit ROX 08 carbon with water was over three times bigger than the rate of imbuing it with alcohol. The imbuing rate was dropping significantly when the SDS solution concentration was increasing.

Layers of Merck coal imbibed water and ethanol at similar rates, which means that this coal is not a perfectly hydrophilic material. For 1, 2 and 5% SDS solutions, the imbuing rate was gradually decreasing with an increase in concentration. At 10% concentration the imbuing rate slightly increased but was still lower than in the case of water.

Also DTO coal was easier to be wetted with water than with ethanol. The rate of imbuing with SDS solutions was much lower, especially at 10% concentration.

Synthetic graphite was slightly easier to be wetted with water than with ethanol. Also in this case the wettability was decreasing with the SDS concentration increase.

The influence of grain size on the rate of imbuing the tested materials' layers with water turned out to be insignificant. 100% grains of Merck active coal were smaller than 0.2 mm (80% smaller than 0.1 mm), and the grains of DTO granulated coal were all larger than 0.2 mm. Both these coals imbibed water at similar rates. Norit ROX 08 coal contained even larger granules, and its layers imbibed water in similar time as synthetic graphite, for which all were below 0.2 mm. However, in the case of Norit R 08 complete saturation with water did not occur. This shows that this coal is of less hydrophilic character.

What results from the condition of equilibrium of capillary and hydrostatic pressures:

$$\frac{2\sigma \cdot \cos\theta}{r} = \rho \cdot g \cdot h, \tag{11}$$

which becomes settled during the capillary rise upwards, is that both water and ethanol should rise to the level of the Norit R 08 EXTRA coal's layer. In the tests presented, only ethanol imbued the layers of Norit R 08 EXTRA, despite the fact that its surface tension is over three times lower than water's. Therefore, there must be another factor causing ethanol to rise higher than water. It is possible that, in the case of such a loose layer, when the radii of porous space channels are large, a significant role is performed by the process of spreading. Spreading is possible when the work of spreading: $W_S = -\sigma \cdot (\cos\theta - 1)$ is negative, that is when $\theta = 0°$. If it is so, the layer of a finer (smaller grains) material should imbibe water easily since in such a case the part of immersion wetting increases — immersion is possible for $\theta < 90°$ (the work of immersion wetting $W_I = -\sigma \cdot \cos\theta$). To confirm this fact, additional tests with grinded Norit R 08 EXTRA coal were performed. Its kinetic specific surface, measured with the Blaine's apparatus, was 4700 cm^2/g. It was formed into layers 1 g in mass, 2.1 cm^3 in volume and with porosity $\varepsilon = 0.76$. Effective diameter of the pores in each layer was approx. 7 μm. The layers were imbued with ethanol, water and SDS water solutions. The time of complete saturation of such layer with water was 6 minutes, with ethanol — 9 minutes. The times of saturation with SDS solutions were increasing with the increase of concentration, up to 13 minutes for the 10% solution. As the tests performed show, the time of saturation with water is shorter than the time of saturation with ethanol. This does not mean that in this case water has better wetting capacities, because in quite a wide range of contact angles the rate of imbuing the capillaries is more heavily dependant on surface tension. From a known formula describing the height of capillary rise h in the time τ [7].

$$h^2 = \frac{r \cdot \sigma \cdot \cos\theta \cdot \tau}{2\eta} \tag{12}$$

the theoretical time of saturating the layer tested with ethanol, assuming perfect wetting ($\theta = 0°$), can be calculated. For the layer's height $h = 1.9$ cm, viscosity of ethanol $\eta = 1.20$ mPa·s, and surface tension 22.8 mN/m [12], the calculated time of saturation with ethanol is 9 minutes, which corresponds to the measurement's result. The same formula can be used to calculate the contact angle of wetting Norit R 08 EXTRA coal with water, substituting the experimental value obtained for the time of complete saturation of the layer with water ($\tau = 6$ min). The viscosity of water is $\eta = 1.00$ mPa·s, and its surface tension $\sigma = 72.8$ mN/m [12]. The calculated contact angle of wetting Norit R 08 EXTRA with water is 66.8°. This confirms the supposition that Norit R 08 coal is less hydrophilic than Norit ROX 08.

The tests showed that all the hydrophilic materials easier imbibed water than SDS solutions. This effect was most visible for the materials that were not finely powdered: Norit ROX 08, DTO. Previous studies do not describe such a significant

influence of SDS presence in water on decreasing the rate of imbuing hydrophilic materials. It was thought that the surfactants adsorption on a material would cause a situation in which near the meniscus there would not be the solution, but water, which is easily imbibed by hydrophilic materials. However, as the tests have shown, the course of imbuing the layers of Norit ROX 08 coal with 5 and 10% SDS solutions, as well as DTO coal with 10% solution, very much resembles the course of imbuing some hydrophobic materials with low concentration solutions, e.g. hard coal with 1% and 2% solutions.

4. 2.   SDS adsorption from water solutions
on the powdered materials tested

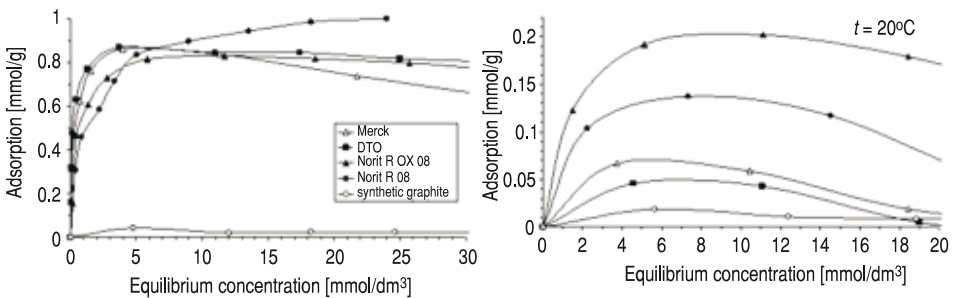The obtained isotherms of SDS adsorption on the tested powdered materials are presented in Fig. 5.

Fig. 5. Isotherm of SDS adsorption from water solutions on the hydrophilic materials tested

Adsorption measurement [13] was not difficult for materials showing strong SDS adsorption, above all active coals. In the case of mineral coals and graphite, some irregularities in the isotherms' courses were noted at high SDS concentrations, when the adsorption values were relatively low. In such cases, it is the heterogeneity of the solid material composition that is important, as well as some specific features of the liquid phase. High concentration water solutions of surfactants are systems complicated to describe. Spherical micelles are transformed into plate ones, and the substances and ions that are transmitted from the solid material to the solution can significantly alter the state of the system [7, 8].

The tests performed showed that the adsorption isotherms for all the materials tested had maxima, except for the adsorption isotherm for Norit R 08 EXTRA coal. The equilibrium SDS concentrations, corresponding to the adsorption maximum, were similar to the value of critical micelle SDS concentration. In the case of the adsorption isotherm for Norit R 08 EXTRA coal, above the concentration 5 mM/dm^3 the increase in the adsorption value was slow. The courses of the

adsorption isotherms for active coals Merck and DTO were almost identical in the range of concentrations lower than those corresponding to the maximum adsorption value. Slightly different were the initial segments of the isotherms for Norit R 08 EXTRA and Norit ROX 08 coals. More profound differences could be observed at higher concentrations (above 10 mM/dm^3). Similar courses of isotherms of alkylsulfates and alkylsulfonates adsorption from water solutions can be found in previous studies on the subject [7, 14, 15, 16, 17].

Among mineral coal materials brown coal had the highest SDS adsorption, followed by peat, Ceylon graphite and hard coal (Fig. 5). Maximum values of SDS adsorption on mineral coals and synthetic graphite were several to twelve times lower than on active coals. This results mainly from the difference of specific surfaces, which for active coals are bigger than for mineral coals by three orders of magnitude. Assuming, on the basis of the previous studies [8], that the surface area occupied in a mono-molecular adsorptive layer of one molecule (for alkyl sulfate) is 0.3 nm^2, the surface area of one gram of the material (S_{DSS}), occupied by the DSS molecules adsorbed, can be calculated:

$$S_{SDS} = \Gamma \cdot 10^{-3} \cdot N_A \cdot 0,3 \cdot 10^{-18} \quad \left[\frac{m^2}{g} \right], \tag{13}$$

where: S_{SDS} — specific surface of the SDS monomolecular adsorptive layer; Γ — adsorption [mM/g]; N_A — Avogadro's number (6.023 · 10^{23}).

The results of these calculations, corresponding to the maximum values of SDS adsorption, are presented in Table 4. This table also contains the values of adsorptive specific surfaces S_a and the relations S_{SDS}/S_a.

TABLE 4

Specific surfaces of the materials tested

	Material	S_{SDS} [m^2/g]	S_a [m^2/g]	S_{SDS}/S_a
Active carbon	Norit R 08 EXTRA	181	1185	0.15
	Norit ROX 08	150	819	018
	Merck	156	1116	0.14
	DTO	157	810	0.19
Synthetic Acheson graphite		7	8.8	0.8
Brown coal		36	1.7	21
Peat		25	1.1	23
Natural Ceylon graphite		14	4.4	3
Hard coal		9	2.9	3
Sulphur		4	0.2	20

The data presented in Table 4 show that multimolecular adsorptive layers are formed on the surface of hydrophobic materials ($S_{SDS}/S_a > 1$). In the case of hydrophilic materials, the values of the relation S_{SDS}/S_a are very low. This can be an indication that on the surface of hydrophilic materials a mono-molecular adsorptive layer is formed.

5. Summary and conclusions

1. Imbuing the layers of coal hydrophobic materials with solutions of surface active substances is a process consisting of two stages: a fast one and a slow one. In the case of layers with small sizes of inter-grain space channels, the rate of imbuing in the slow stage is low and practically does not depend on the solution's concentration.

2. The inhibition of the process of imbuing hydrophobic materials layers with SDS solutions is caused by the adsorption of the surface active compound's molecules on the materials' surface. As a result, the concentration of the solution decreases and so do its wetting capacities. SDS forms multimolecular adsorptive layers on the surface of hydrophobic materials. This may cause a decrease in the solution concentration in the area of the liquid's shifting meniscus almost to zero, and an increase in the wetting contact angle up to 90°.

3. The rate of imbuing hydrophilic materials layers with surfactant solutions is lower than the rate of imbuing them with water, and it usually decreases with the increase of solution concentration. The influence of grain size on the rate of imbuing hydrophilic materials is insignificant.

4. Using surface active substances in fire fighting, therefore, to improve the wetting capacities of water, makes sense only in the case of surface fires and fires of loose layers, that is in situations when the decisive factor is adhesive wetting.

5. Applying surface active substances in situations when it is capillary forces that determine the rate of water absorption, e.g. subsurface fires of hydrophobic materials, is of no advantage, while it raises the costs of action, increases the fire losses and damages the environment. In the case of fires the firebrand of which is situated deep down, it can be stated that surfactants will not make the fire-fighting action any faster. When the layer imbibes the solution slowly, the rate of water evaporation from the solution front will be higher than the rate of its migration deep into the layer.

6. Using surface active substances to improve the wettability of hydrophilic materials is always inadvisable. In the case of porous materials the wettability worsens as a rule. The potential shortening of the time of action when fighting surface fires is an insufficient argument, if one takes into account the costs

of applying surface active substances, environmental damage, or additional burden on sewage treatment plants.

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A. MIZERSKI, S. NEFFE

Badania nasiąkania i właściwości zwilżających wodnych roztworów siarczanu dodecylo sodu na porowatych złożach materiałów hydrofilowych i hydrofobowych

Streszczenie. Przeprowadzono badania kinetyki nasycania porowatych warstw różnych materiałów za pomocą wodnych roztworów dodecylosiarczanu sodu. Badania wykonano dla następujących materiałów: czterech rodzajów węgli aktywnych: Norit R 08 EXTRA, Norit ROX 08, DTO i Merck; trzech rodzajów węgli kopalnych: węgla kamiennego, węgla brunatnego i torfu; dwóch rodzajów grafitów: naturalnego grafitu cejlońskiego, syntetycznego elektrografitu oraz sproszkowanej siarki. Kinetykę nasycania badano metodą wznoszenia kapilarnego, przy zastosowaniu przepływu cieczy od dołu do góry. Wyniki przedstawiono w formie zależności stopnia nasycenia warstw od czasu ich nasycania. Zbadano również wpływ adsorpcji dodecylosiarczanu sodu na kinetykę zwilżania warstw badanych materiałów. Uzyskane wyniki wykazały, że węgle kopalne, grafit naturalny i siarka trudno zwilżały się badanymi roztworami substancji powierzchniowo czynnych. Natomiast węgle aktywne i syntetyczny elektrografit były w różnym stopniu hydrofilowe i miały wysoki współczynnik nasycania. Wyniki badań zostały przedyskutowane pod kątem możliwości ich wykorzystania w technologii gaszenia podpowierzchniowych pożarów węglowych materiałów porowatych.

Słowa kluczowe: zjawiska powierzchniowe, substancje powierzchniowo czynne, technologie przeciwpożarowe