

## Distribution of adhesion rate constant in the coal sample

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### Rozdelenie rýchlostných adhézných konštánt v uhoľnej vzorke

Flotation is the process of enrichment which consists in differentiating the useful component (volume property) in the separation products. Flotation leads to the differentiation of the volume property by means of applying the differentiation of surface properties. Since there is a correlation between these properties, the authors determined the distribution of adhesion rate constant in relation with the content of the useful component and applying the dispersive model of a particle. The content of the useful component is directly connected with the volume physical property, represented by particle density.

The paper present distribution functions of density and adhesion rate constant in the sample. Also the relation between adhesion rate constant and ash content for narrow density fractions has been revealed.

**Key words:** flotation kinetics, physical model of particle, adhesion rate constant, distribution of adhesion rate constant

### Introduction

The flotation properties of a particle are determined by surface properties of particles which can be modified by means of flotation reagents within a certain range.

In the macroscopic, approach the bubble mineralization is a result of two events, i.e. the collision of a particle with a bubble and the adhesion of the particle to the bubble surface. Both these events are of a random character and the process of flotation can be considered as a stochastic process. Apart from the above events, the already attached particles can be detached from the bubble surface by the external collateral forces in the flotation chamber, which are generated by the medium turbulences. This process is also of a random character. From the point of view of mathematics, the stochastic process which considers the phenomenon of adhesion and detachment particles from the bubble surface is called the process of birth and death (Bailey, 1964; Stachurski, 1972). In this model, the random variable is constituted by a number of particles elevated by a bubble to the layer of froth to the time  $t$ . The intensity of the process of adhesion and detachment is characterized by the function of adhesion process intensity  $\lambda(l)$  and the function of detachment process intensity  $\mu(l)$ . These functions are expressed by the following formulas:

$$\lambda(l) = \lambda_0 (n_0 - l) \quad (1)$$

$$\mu(l) = \mu_0 l \quad (2)$$

where  $n_0$  is the total number of particles under flotation in the flotation chamber in the moment  $t=0$ ,  $l$  is the number of particles attached to bubbles,  $\lambda_0$  is the adhesion rate constant and  $\mu_0$  is the detachment rate constant. It results from the above formulas that the adhesion process intensity is proportional to the number of particles remaining in the suspension ( $n_0 - l$ ) whereas the tearing off process intensity is proportional to the number of particles attached to bubbles ( $l$ ).

Solving the system of differential equations of the process of birth and death, we obtain the expression for the recovery of floatable particles, elevated to the froth layer  $\varepsilon(t)$  to the time  $t$ :

$$\varepsilon(t) = \frac{\lambda_0}{\lambda_0 + \mu_0} \left[ 1 - e^{-(\lambda_0 + \mu_0)t} \right] \quad (3)$$

where  $\varepsilon$  is the recovery of the considered particles in the froth product and  $\varepsilon_\infty = \frac{\lambda_0}{\lambda_0 + \mu_0}$  is the equilibrium recovery.

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It results from the equation (3) that:

$$\lim_{t \rightarrow 0} \frac{d\varepsilon}{dt} = \lambda_0 \quad (4)$$

The particle surface properties and physicochemical conditions in the flotation chamber determine the value of the adhesion rate constant.

Flotation is the process of enrichment, which consists in differentiating the content of a useful component in separation products. The content of the useful component is a volume property. Therefore, as a result of flotation, the differentiation of the volume property occurs by the differentiation of surface properties. There should be a relation between particle volume properties and particle surface ones. Moreover, a hypothesis can be put forward that a distribution of surface (hydrophobic) properties of particles in the sample should be related with a distribution of volume properties. In the case of coal, this relation can be deduced in the following way. The particle surface properties depend on the exposition rate of mineral matter on the particle surface which, subsequently, depends on the content of this matter in the particle. On the other hand, however, the rate of covering the particle surface with a collector and adhesion effectiveness decrease; thus adhesion rate constant decreases, too. Therefore the distribution of adhesion rate constant in a sample will depend on the distribution of the mineral matter content.

Assuming that the mineral matter is evenly distributed in the volume of a spherical particle of radius  $R_p$ , the total content of mineral matter in the sphere of radius  $r$  ( $r \leq R_p$ ) and thickness of infinitely small sphere  $dr$  will be equal to:

$$d\lambda = \lambda 4 \pi r^2 dr \quad (5)$$

where  $\lambda$  is the volume content of the mineral matter in the particle.

If  $r = R_p$ , it can be assumed that the exposition rate of mineral matter on the particle surface or, in other words, the surface content of mineral matter on the particle surface  $\omega$  will be:

$$\omega = \frac{d\lambda}{4\pi R_p^2} = \lambda dr \quad (6)$$

The surface content is thus proportional to the volume content of mineral matter in the particle. The larger the surface content of mineral matter, the lower the effectiveness of adhesion.

The adhesion rate constant decreases with the growth of ash content  $A$ , according to the following dependence:

$$\lambda_o(A) = a e^{-b A} \quad (7)$$

where  $a$  represents the adhesion rate constant for pure coal (which is depends on the type of coal), the degree of oxidation and the previous treatment by other reagents,  $b$  is a constant.

From formula (7), the reciprocal dependence, of the ash content on the adhesion rate constant is obtained as follows:

$$A = \frac{1}{b} \ln \frac{a}{\lambda_o} \quad (8)$$

#### Distribution function of adhesion rate constant

The distribution of adhesion rate constant in a sample depends on the distribution of the content of mineral matter while the distribution of mineral matter content is determined according to the particle dispersion model (Brożek 1995b,1995c). In this model, the mineral raw materials are treated as a multi-phase system and a phase is a part of the medium which is homogeneous from the point of view of physical and chemical properties. (Cottrell 1964). A continuous phase and a dispersed one are differentiated in the two-component dispersive system. In the case of coal the continuous phase is constituted by the organic coal matter while the dispersed phase by the dissemination of mineral matter. It is assumed in the dispersive model that the number of disseminations of the dispersed phase in the particle of volume  $V$  is a random variable  $s(V)$  of the Poisson frequency function.

The cumulative distribution function of the Poisson distribution is expressed by the incomplete gamma function, also known as the Pearson function (Gradstein et.al, 1971):

$$F(s) = \frac{1}{\Gamma(1+s)} \int_{nV}^{\infty} e^{-t} t^s dt = I(nV; 1+s) \quad (9)$$

where  $\Gamma(1+s)$  is the gamma function,  $I(nV; 1+s)$  is the Pearson's function (Firkowicz 1970). Subsequently, the following Pearson's function constitutes the cumulative distribution function of the dispersed phase content:

$$F(A) = I(H A_p; 1 + H A) \quad (10)$$

where  $A_p$  represents the average volume content of the dispersed phase in the sample whereas  $H$  is a constant connected with the size of a particle and disseminations.

Substituting the dependence (8) into (10) we obtain the expression for a cumulative distribution function of the adhesion rate constant:

$$F(\lambda_o) = 1 - I(B_1; 1 + B_2 \ln \frac{a}{\lambda_o}) \quad (11)$$

where:  $B_1 = H A_p$  and  $B_2 = H/b$  are parameters of the distribution connected with the distribution of disseminations and particle sizes, respectively.

## Experimental method

### Sample preparation

Coal type 33 was used which was crushed in a roll crusher to below 0,5 mm. The wet sieve analysis was performed, achieving the (0,315-0,2) size fraction, followed by the float and sink analysis. The analysis was carried out in the zinc chloride solutions and its products were washed carefully with warm water. The following density fractions – (-1,35), (1,35-1,5), (1,5-1,7), (1,7-1,8), (1,8-2,0) (+2,0), were selected in order to ensure the appropriate amount of the raw material for planned experiments according to the analysis of separation product yields in heavy liquids. The ash content was denoted within the obtained narrow density fractions and according to the Polish standard. The test samples were vacuum-stored to prevent a possible oxidation of the coal surface.

### Determining the flotation kinetics

Flotation experiments for coal were carried out at the room temperature in the Denver type laboratory machine of 1 dm<sup>3</sup> chamber capacity, at the constant number of rotational speed of 2020 [min<sup>-1</sup>] and the fixed air consumption. The content of solids was the same in all experiments, i.e. 80 g /dm<sup>3</sup>. Such conditions ensured the constant amount and size of air bubbles in the chamber at a limited turbulence of the flotation pulp caused by the rotator action. The low concentration of flotation pulp was determined by practical reasons because at a low concentration of the pulp it is possible to achieve favorable results of coal flotation (Sablík, 1998). Water solutions of n-butanol were used as the collecting and frothing reagent. These solutions do not change pH of the pulp but only decrease the surface tension on the gas-liquid boundary and the air dispersion in the suspension grows. Also, the adsorption of alcohol on the surface of air bubbles occurs which ensures its stabilization and prevents coalescence (Małysa, 2000; Krzan et.al. 2002). On the basis of introductory investigations, the authors choose appropriate values of the reagent concentration which guaranteed the formation of froth of proper structure and durability. The samples were dried and weighed and the ash content was measured. The obtained results were used to determine the distribution of the adhesion rate constant.

## Distribution of adhesion rate constant

### Distribution of density and ash content in the sample

A prior float and sink analysis of the coal sample was performed in order to determine the density distribution of the distribution of the adhesion rate constant. The distribution function of density in the tested sample was drawn according to the obtained result for the sample of particle size (0,2–0,315) mm in which the consecutive densimetric fractions differ significantly in the ash content, i.e. in the content of mineral matter (which means that they should differ in their flotation properties). The cumulative distribution function of density is expressed by the incomplete gamma function (Brožek, 1995b,c):

$$F(\rho) = I[K_1; 1 + K_2 (\rho - \rho_0)] \tag{12}$$

where  $K_1$  and  $K_2$  are the distribution parameters. Figure 1 presents a model cumulative distribution function of density (the continuous line) together with the experimental point. The equation of this distribution function in the range of particle density ( $\rho_{min}, 2,0$ ) is as follows:

$$F_1(\rho) = 0,83 [0,94 I(2,2; 1 + 30 (\rho - 1,3))] \tag{13}$$

where the density  $\rho$  is expressed in  $[Mg/m^3]$ .

Parameters  $K_1$  and  $K_2$  were determined from the table of the incomplete gamma function (Pagurova, 1963) by the method of gradual approaching situation in which, for a given value of  $K_1$ ,  $K_2$  reaches a value at which the index of curvilinear correlation is maximum. For the dependence (13), the index of the curvilinear correlation is larger than 0,95. For the density of particles above  $2,0 Mg/m^3$ , no detailed float and sink analysis was performed. Nevertheless, as the experiment shows (Brożek, 1995b,c), the distribution of the mineral matter content in this range of particle density is also expressed by the incomplete gamma function, but with the parameters different from those in the distribution below  $2,0 Mg/m^3$ . Consequently, for the entire range of particle density the cumulative distribution function of density is expressed by the formula:

$$F(\rho) = \Phi_1 F_1(\rho) + \Phi_2 F_2(\rho) H(\rho - 2,0) \tag{14}$$

where  $F_1$  and  $F_2$  are cumulative distribution functions, respectively, for the ranges of particle densities below and over  $2,0 Mg/m^3$ ,  $H$  is Heaviside's function (Byron et.al. 1975),  $\Phi_1$  and  $\Phi_2$  are particle fractions of density below and over  $2,0 Mg/m^3$  in the sample ( $\Phi_1 + \Phi_2 = 1$ ).

The graph of distribution function  $F_2(\rho)$  is of a pictorial character in Fig. 1. It can be seen from the form of the formula (14) that the density in the sample is a bi-modal distribution. The dependence between the density and the mass content of ash in particle  $A$  was determined to find the distribution function of ash. The general form of this dependence is as follows:

$$A(\rho) = c_1 - \frac{c_2}{\rho} \tag{15}$$

where  $c_1$  and  $c_2$  are constants connected with the density of organic coal matter and the average density of mineral matter (Brożek 1995a). The detailed form of this dependence is as follows:

$$A(\rho) = 1,54 - \frac{2}{\rho} \tag{16}$$

where the density  $\rho$  is expressed in  $Mg/m^3$  and  $A$  has fractional values

Fig. 2. presents the dependence of the ash content on the density reciprocal of the fraction. The linear correlation coefficient is larger than 0.98. From the formula (16), the dependence of the density upon the ash content in the particle is expressed by the formula:

$$\rho = \frac{2}{1,54 - A} \tag{17}$$

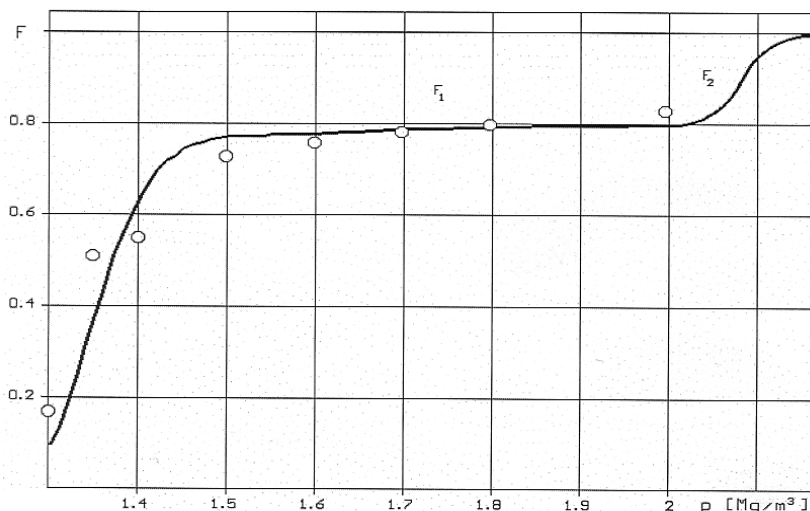
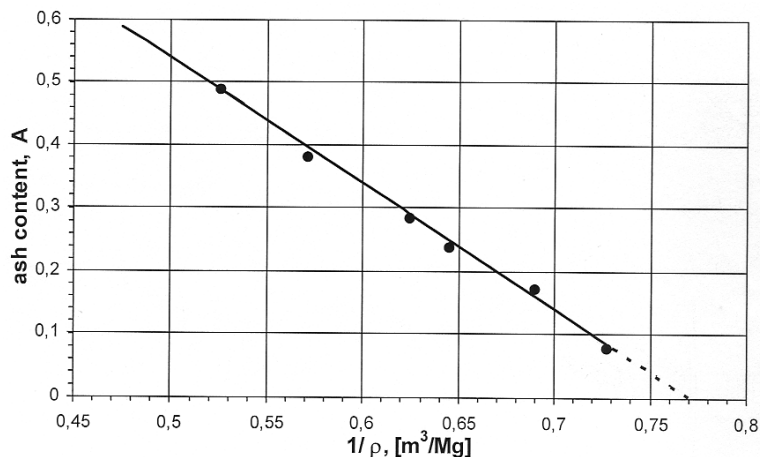


Fig. 1. Cumulative distribution function of the density in the tested sample

Fig. 2. Dependence of the ash content on the density reciprocal of the fraction



After substituting expression (17) into (13), we may obtain the form of the cumulative distribution function of the ash content for the range of particle density below 2,0 Mg/m<sup>3</sup>:

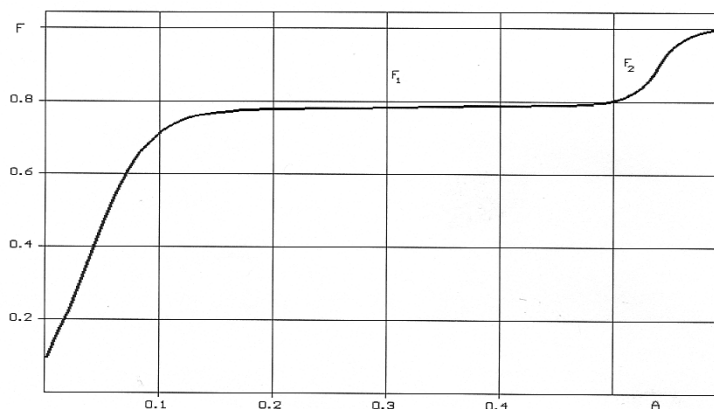
$$F_1(A) = 0.83 \left[ 0.94 I \left( 2.2; 1 + \frac{39 A}{1.54 - A} \right) \right] \quad (18)$$

While for the entire range of particle density:

$$F(A) = \Phi_1 F_1(A) + \Phi_2 F_2(A) H(A - 0.54) \quad (19)$$

The shape of the distribution function  $F(A)$  is analogous to  $F(\rho)$  and is shown in Fig. 3.

Fig. 3. Distribution function of the ash content for the particle density below 2,0 Mg/m<sup>3</sup>:



### Flotation kinetics of densimetric fractions

Investigations of the flotation kinetics of respectively densimetric fractions were performed at the butanol concentration of  $2 \cdot 10^{-3} \text{ mol/dm}^3$  and the corresponding surface tension of solution of 68,5 [mN/m].

Curves of the flotation kinetics were drawn according to the obtained results of cumulated recoveries of the combustible and volatile matter in the froth product at the flotation time  $t$ . The empirical dependences were approximated by the model equations of the flotation kinetics of 1-st order (equation 3). The parameters of this equation,  $\varepsilon_\infty$  and  $k = \lambda_0 + \mu_0$  were calculated by applying the least square method for the given value  $\varepsilon_\infty$ . The rate of consistency of the model dependence with the empirical courses was evaluated by means of the curvilinear correlation index  $R$ . The value  $\varepsilon_\infty$  were changed by 0,01 to reach the maximum value by the curvilinear correlation index. Fig. 4-10 show model curves of flotation kinetics. The empirical values are marked with the circles. In all cases the curvilinear correlation index is larger than 0,96.

The adhesion rate constant was calculated according to the model dependence  $\varepsilon(t)$  according to the formula:

$$\lambda_0 = \lim_{t \rightarrow 0} \frac{d\varepsilon(t)}{dt} = k \varepsilon_\infty \quad (20)$$

The model dependence  $\varepsilon(t)$  and the value of the adhesion rate constant  $\lambda_0$  calculated, are given for all graph. Fig. 10. shows the dependence of adhesion rate constant on the ash content in the sample subjected to flotation. This dependence, according to formula (7), is as follows:

$$\lambda_0(A) = 0.15 e^{-2A} \quad (21)$$

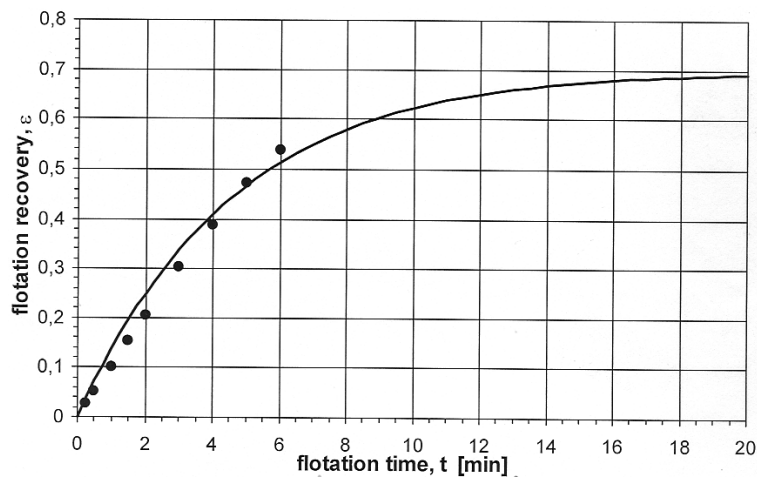


Fig. 4. Flotation kinetics of the fraction  $<1,35 \text{ Mg/m}^3$ , ( $\varepsilon = 0,70(1 - e^{-0,22t})$ ,  $\lambda_0 = 0,154 \text{ 1/min}$ )

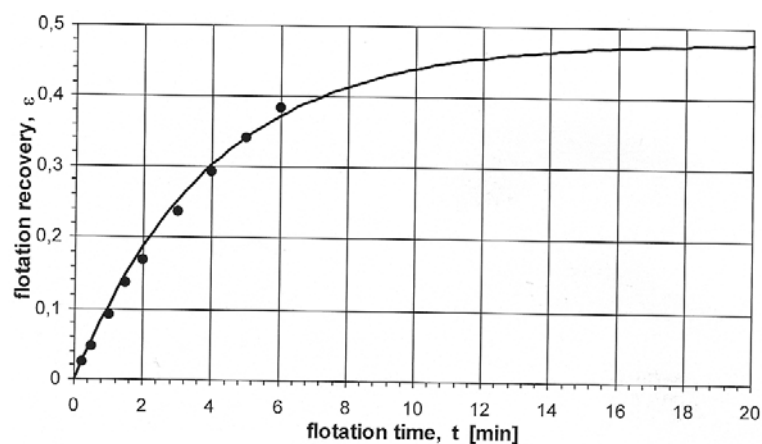


Fig. 5. Fractional kinetics of the fraction  $1,35-1,5 \text{ Mg/m}^3$ , ( $\varepsilon = 0,48(1 - e^{-0,249t})$ ,  $\lambda_0 = 0,12 \text{ 1/min}$ )

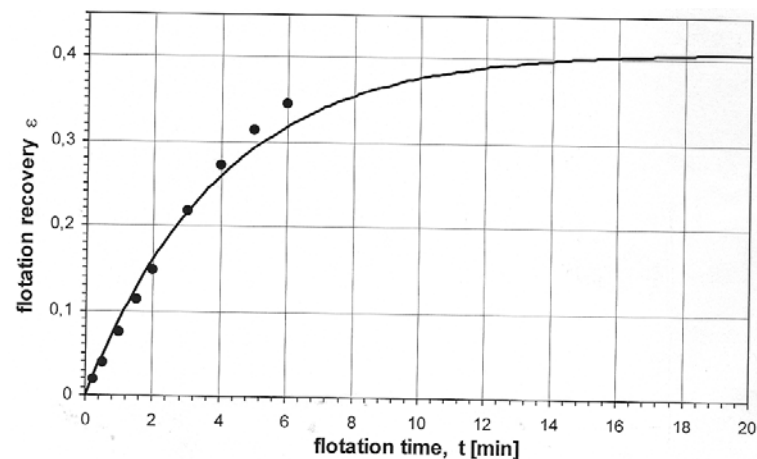


Fig. 6. Fractional kinetics of the fraction  $1,5-1,7 \text{ Mg/m}^3$ , ( $\varepsilon = 0,41(1 - e^{-0,25t})$ ,  $\lambda_0 = 0,102 \text{ 1/min}$ )

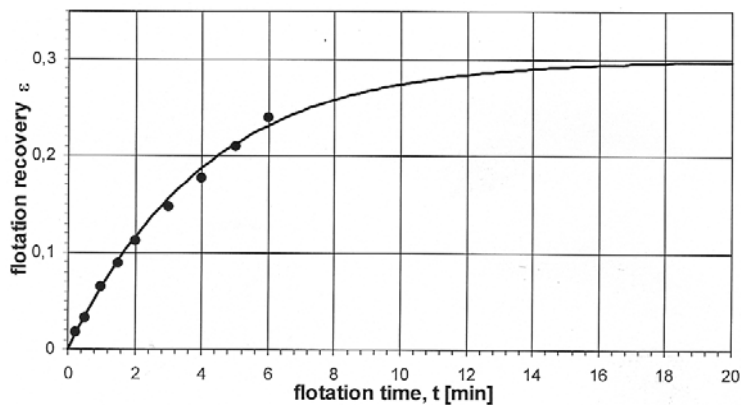


Fig. 7. Fractional kinetics of the fraction  $1,7-1,8 \text{ Mg/m}^3$ , ( $\varepsilon = 0,30(1 - e^{-0,246t})$ ,  $\lambda_0 = 0,074 \text{ 1/min}$ )

Fig. 8. Fractional kinetics of the fraction 1,8-2,0 Mg/m<sup>3</sup>, ( $\varepsilon = 0,20(1 - e^{-0,245t})$ ,  $\lambda_0 = 0,079$  1/min)

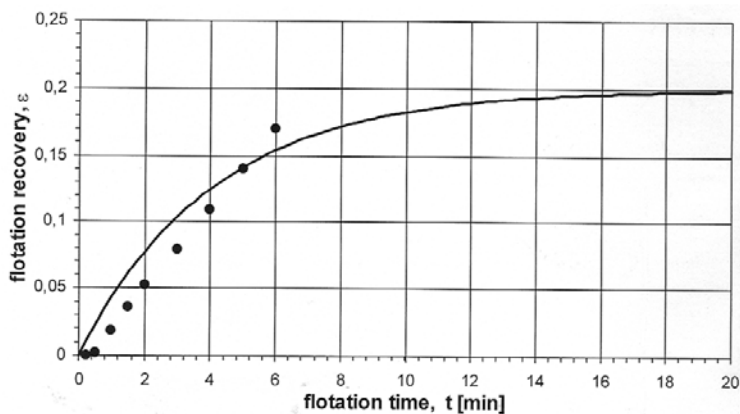


Fig. 9. Fractional kinetics of the fraction >2,0 Mg/m<sup>3</sup>, ( $\varepsilon = 0,12(1 - e^{-0,249t})$ ,  $\lambda_0 = 0,03$  1/min)

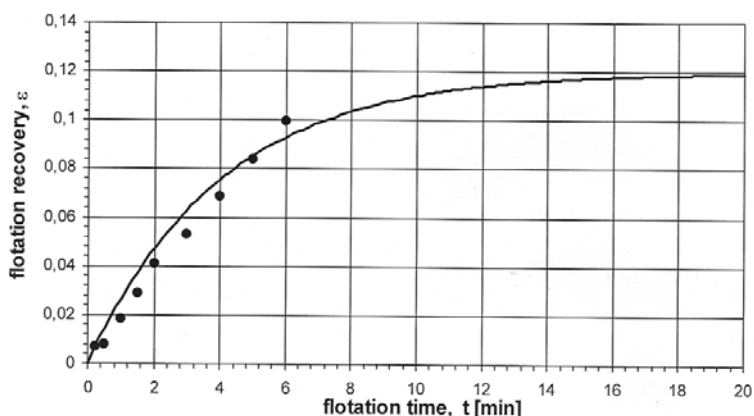
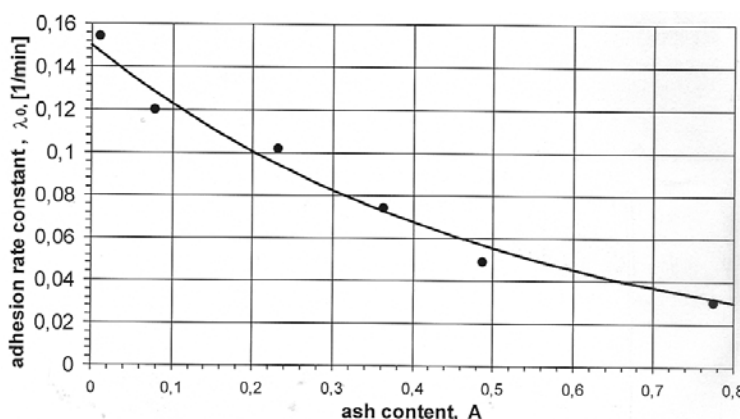


Fig. 10. Adhesion rate constant as the function of the ash content in the sample; ( $\lambda_0 = 0,15 e^{-2A}$ ).



The curvilinear correlation index is 0,9999022, which proves a very good consistency of the proposed model dependence with the experimental values.

**Cumulative distribution function of adhesion rate constant**

The ash content, according to the formula (21), is:

$$A = \frac{1}{2} \ln \frac{0.15}{\lambda_0} \tag{22}$$

Substituting the above dependence into formula (18), we obtain the distribution function rate constant of adhesion for the particle density below 2.0 Mg/m<sup>3</sup>:

$$F_1(\lambda_0) = 1 - 0.83 \left[ 0.87 I \left( 2.2; \frac{-38 \ln \lambda_0 - 69}{\ln \lambda_0 + 5} \right) \right] \tag{23}$$

The graph of the function (23) is presented in Fig. 11. together with the experimental values. The curvilinear correlation index is larger than 0.95. Analogously, as in the case of the distribution function of the density and mineral matter content, the distribution function of the adhesion rate constant for the entire range of variability λ<sub>0</sub> is expressed by the formula:

$$F(\lambda_0) = \Phi_1 F_1(\lambda_0) + \Phi_2 F_2(\lambda_0) H(\lambda_0 - 0.04) \tag{24}$$

Analogously, the frequency function is as follows:

$$f(\lambda_o) = \Phi_1 f_1(\lambda_o) + \Phi_2 f_2(\lambda_o) \quad (25)$$

Fig. 12. shows the frequency function of the adhesion rate constant (the first part of the dependence  $f_2(\lambda_o)$  is of a pictorial character). It is, therefore, a bi-modal distribution.

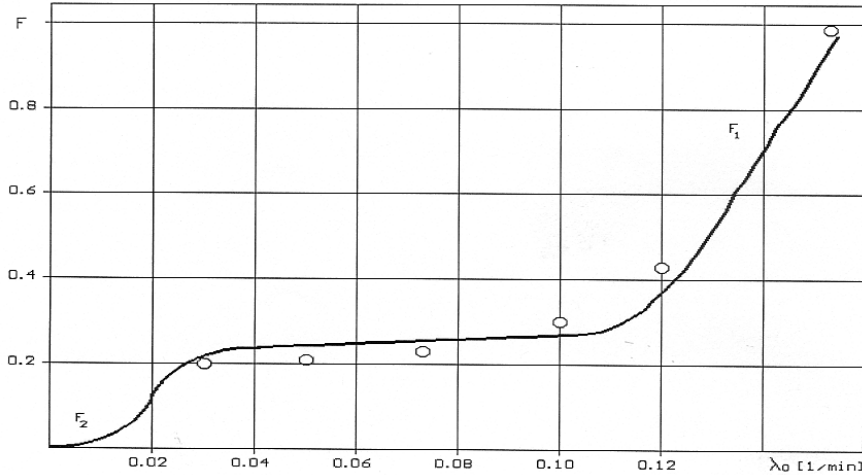


Fig. 11. Distribution function of the adhesion rate constant for the particle density below  $2.0 \text{ Mg/m}^3$

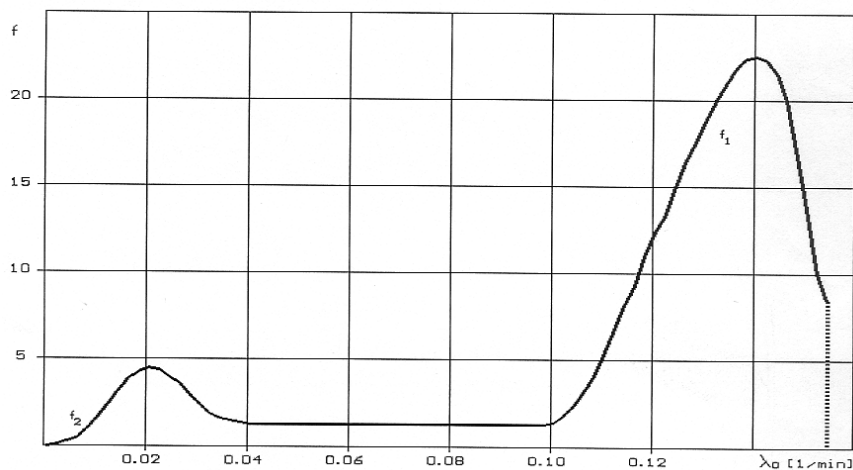


Fig. 12. Frequency functions of the adhesion rate constant, the dependence  $f_2(\lambda_o)$  is of the pictorial character.

The bi-modal distribution of the flotation rate constant was proposed by Kalinowski and Kaula (1994). Such a type of distribution results from the character of distribution of the mineral matter content in coal. It can be, therefore, only grounded by combining the flotation properties of particles with the mineral matter content.

### Conclusions

1. Basing on the assumption of existence of a relation between surface and volume properties of a particle, a distribution of the adhesion rate constant was determined on the ground of a physical model of the particle. This distribution is correlated with the distribution of the mineral matter content. Only on the grounds of this model it is possible to justify the application of the bi-modal distribution in the flotation kinetics of non-homogeneous materials from the point of view of flotation properties.

2. Hydrodynamic conditions in a given flotation machine affect the values of adhesion rate constant, calculated from the equation of flotation kinetics and also its distribution, beside the physicochemical conditions in the flotation chamber. To make the distribution of flotation properties in the sample objective, the authors would have to assume the magnitude to be a measure of these properties whose value depends on the physicochemical conditions of the flotation medium and on the distribution of surface properties, (conditioned by the content of the component under flotation). It seems that, the critical wetting surface tension could be such a measure for grained materials, since such a method can determine the distribution of this property in the sample without its prior processing with other chemical reagents, (such as zinc chloride solutions in the float and sink analysis, applied to separate narrow density fractions). Such



investigations are planned and their results will determine a choice of the measure of floatability of grained materials, (non-homogeneous from the point of view of volume properties).

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