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THE EFFECT OF SURFACE-ACTIVE COMPOUNDS ON THE TENSILE STRENGTH OF LIMESTONE AND PORPHYRY PARTICLES

WPŁYW ZWIĄZKÓW POWIERZCHNIOWO CZYNNYCH NA WYTRZYMAŁOŚĆ NA ROZCIĄGANIE ZIAREN WAPIENIA I PORFIRU

The real strength of solids is affected by the presence of structural defects, i.e. micro-cracks around which the stresses during tension are concentrated. It depends also on the free surface specific energy, which can be reduced by the introduction of surface active compounds (SAC).

This paper presents the results of investigations on the influence of surface-active compounds upon the tensile strength of single mineral particles. The tests were performed on limestone and porphyry. The authors determined the distribution of strength of particles without chemical treatment and after treatment with distilled water and solutions of sodium oleate and dodecylamine hydrochloride. The effect of SAC was evaluated according to the average tensile strength value and the wetting angle, determined by the settled drop method.

The results indicate that different substances have varied effects in lowering the strength of limestone and porphyry particles. These differences can be explained by the different SAC adsorption rates on the surface of each material which, in consequence, result in different penetration rates in primary micro-cracks (on which the amount of crack-strength lowering depends). It can also be explained by the different number of surface cracks on limestone and porphyry particles. This hypothesis is confirmed by the results of investigations of the wetting angle of both materials by the surface active compounds used in this investigation.

Key words: particle tensile strength, surface-active compounds, Weibull's distribution, wetting angle

Rzeczywista wytrzymałość ciał stałych jest uwarunkowana obecnością wrodzonych wad struktury — mikropęknięć, wokół których koncentrują się naprężenia przy rozciąganiu. Jest ona również zależna od swobodnej energii powierzchniowej właściwej, którą można obniżyć za pomocą związków powierzchniowo czynnych (ZPC).

Praca przedstawia wyniki badań wpływu ZPC na wytrzymałość pojedynczych ziaren mineralnych na rozciąganie. Badania wykonano na wapieniu i porfirze. Wyznaczono rozkład wytrzymałości ziaren

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bez obróbki chemicznej, a także po obróbce wodą destylowaną oraz roztworami oleinianu sodu i chlorowodorku dodecyloaminy.

Wpływ ZPC oceniano na podstawie średniej wartości wytrzymałości na rozciąganie oraz kąta zwilżania wyznaczonego metodą osadzonej kropli.

Dystrybuantę rozkładu wytrzymałości ziaren dobrze przybliża rozkład Weibulla. Dobroć dopasowania mierzono wskaźnikiem Q określonym wzorem (9). Szczegółowe postacie rozkładów wytrzymałości przedstawiają wzory (11)–(18). Sądząc z wartości wskaźnika Q, rozkład Weibulla dobrze przybliża rozkład wytrzymałości na rozciąganie nieregularnych ziaren mineralnych.

Wartości wytrzymałości średniej $\overline{\sigma}$ oraz średni procentowy spadek wytrzymałości ziaren po obróbce ZPC $\Delta\overline{\sigma}/8{,}3$ oraz $\Delta\overline{\sigma}/7{,}58$ odpowiednio dla wapienia i porfiru przedstawia tablica 1.

Zarówno w przypadku wapienia, jak i porfiru stosowane ZPC obniżają wytrzymałość ziarna. Jednakże stopień obniżenia wytrzymałości na rozciąganie za pomocą tego samego związku jest zróżnicowany. W przypadku wapienia, który jest materiałem jednorodnym, największe obniżenie wytrzymałości uzyskuje się po obróbce roztworem aminy, natomiast w przypadku porfiru, który jest materiałem niejednorodnym, analogiczny spadek wytrzymałości zanotowano po obróbce wodą destylowaną. To zróżnicowanie spadku wytrzymałości ziaren wapienia i porfiru po obróbce tymi samymi związkami znajduje wyjaśnienie w wartościach kąta zwilżania obu surowców przez ten sam ZPC (według wzorów Younga (19) i Griffith'a (1) większy kąt zwilżania pociąga za sobą większą wytrzymałość ziarna). Kąt zwilżania jest zależny od rodzaju stosowanego odczynnika (tabl. 1). Jak widać z tablicy 1, im większy kąt zwilżania tym większa wytrzymałość ziaren wapienia. Zatem przez pomiar kąta zwilżania można oceniać wielkość wpływu ZPC na obniżenie wytrzymałości materiałów jednorodnych. W przypadku materiałów niejednorodnych wartość kąta zwilżania przez różne związki nie musi pozostawać w takiej samej korelacji z wartościami wytrzymałości średniej ziaren, gdyż wtedy działanie ZPC jest zależne najprawdopodobniej od składu mineralnego danego materiału. Wynika to z faktu, że mechanizm działania ZPC i stopień ich adsorpcji w szczelinach znajdujących się na granicach faz mineralnych może być zależny od rodzaju sąsiadujących minerałów. Hipotezy te wymagają jednak potwierdzenia na przykładzie innych materiałów jednorodnych i niejednorodnych. Ponieważ woda jest związkiem silnie zmniejszającym wytrzymałość niektórych ciał stałych, celowe jest przebadanie wpływu stężenia ZPC na obniżenie wytrzymałości.

1. Introduction

The effect of surface interactions in the comminution process is revealed in two ways. Firstly, the physical adsorption of surface-active compounds leads to a change of particle strength. Secondly, as the particle size decreases and their relative overall surface area increases, the forces of mutual interaction between particles intensifies. These interactions lead to the coagulation of the dispersed particles and decrease the efficiency of the grinding process (Shulze 1992).

The theoretical tensile strength of a solid is related to its crystalline structure. As can be observed, the theoretical tensile strength, resulting from breaking the atomic bonds in the ideal crystal, is 10^2–10^4 times larger than the strength when measured under test conditions. Griffith (Griffith 1921) formulated a hypothesis to explain this discrepancy, which stated that in every solid there are tiny cracks which decrease the body strength. According to Griffith, the tensile strength of the solid weakened by a lenticular crack $2a$ long is:

$$\sigma = \sqrt{\frac{2E\gamma}{\pi a}} \qquad (1)$$

where:

γ — free surface specific energy,

E — Young's modulus.

In brittle bodies which comprise the majority of raw mineral materials primary microcracks and structural defects such as dislocations are present. These concentrate stresses when the material is subject to tension. Additionally, such cracks tend to form in the surface layer initially, at the contact boundary of the particle to be crushed with a compressive or impacting object. The particle strength and comminution probability depend on the number of micro-cracks and fissures, whilst the specific comminution energy is equal to (Bergstrom et al. 1961; Kanda et al. 1986; Austin 1987):

$$W_m = \frac{0.897}{9}\pi^{2/3}\left(\frac{1-\nu}{E}\right)^{2/3}\sigma^{5/3} \qquad (2)$$

where:

ν — Poisson's ratio.

Therefore the particle strength should be reduced in order to decrease the comminution energy.

Formula (1) shows that tensile strength of a solid depends on free surface energy. The decrease of surface energy results in lowering the particle strength. This reduction in surface energy can be effected by applying surface-active compounds (SAC) which, when adsorbed on the surface of the solid, change its mechanical properties.

The lowering of surface energy may also occur as a result of electrical surface polarization, a chemical reaction on the surface or especially by introducing a liquid medium of comparable molecular construction to the solid surface. The effect of reducing the strength of solids as a result of SAC adsorption is known as *Rebinder's Effect* (Percov et al. 1970). This effect can occur in all bodies, whether crystalline or amorphous, continuous or porous, with ionic, covalent or metallic bonds. The magnitude of this effect depends on many thermodynamic and kinetic factors, such as the character of inter-atomic interactions inside the solid (chemical composition, durability of bonds, structure of the crystalline lattice), inside the liquid and on the phase-boundaries, the physical structure of the solid in respect of structural defects (grain boundaries, dislocations and other flaws), conditions of processing (temperature, load velocity, speed of SAC penetration into the stress concentration zone).

2. The mechanism of SAC action in the process of comminution

The analysis of the SAC effect on the process of comminution can be considered at both macro- and microscopic levels.

When explaining the effect of SAC on the process of comminution from the macroscopic point of view, the phenomena occuring on the phase boundaries should be taken into consideration. The solid molecules on the phase boundary, as opposed to the internal molecules, are subject to the action of forces whose resultant is directed towards the core of the body. These non-saturated forces act on the liquid phase molecules, which leads to their concentration on the phase boundary, i.e. to adsorption. The physical adsorption is dependant on Van der Waals interactions, which take place when the liquid molecules approach the solid surface.

Growth of the gross boundary surface area takes place during the process of comminution. The work performed to increase the boundary surface by dA is:

$$dL = \gamma_{SV} dA \tag{3}$$

where γ_{SV} represents the surface tension (specific surface energy) on the solid/gas phase boundary. If comminution takes place in the liquid medium, then:

$$dL = \gamma_{SL} dA \tag{4}$$

where γ_{SL} is the surface tension on the solid/liquid phase-boundary. Since $\gamma_{SV} > \gamma_{SL}$, to produce the same comminution level in a liquid medium requires less energy than in a gaseous medium. The reduction in required energy is equal to:

$$dL = (\gamma_{SV} - \gamma_{SL})dA \tag{5}$$

Estimated calculations show that the maximum lowering of the surface energy of a solid is in the $\Delta L \cong RT\Gamma_m$ range, where Γ_m presents maximum adsorption, R is the universal gas constant and T is the temperature in Kelvin. Since the value of maximum adsorption is of the order of 10^{-9} mol/cm^2, the maximum decrease of surface energy of the solid body is of the order of several tens of erg/cm^2 (Percov et al. 1970).

Analysing the SAC action on the process of comminution at microscopic level, the effect of such compounds on the particle strength should be taken into acount. As evinced by experience, the particle strength is significantly affected by various defects and surface micro-cracks, because the process of particle destruction begins from the surface layers. When a load is applied, under the influence of tensile stresses, the micro-cracks tend to open up. After removing the stresses (within the limits of material elastic strains) the cracks close up again under the effect of the intermolecular cohesion forces.

Fig. 1 presents a wedge-shaped micro-crack. If the process of loading occurs in the presence of SAC, the SAC molecules migrate inside the crack on its internal surfaces, blocking the action of the cohesive forces. This causes a lowering of surface energy and the appearance of additional pressure P_b, facilitating further development of the micro-crack, under the fixed external load. This is equivalent to the growth of loading by a certain value dF, expressing the mechanical action of the SAC adsorption layer. When

SAC are adsorbed from the liquid lubricating the solid, under the effect of capillary pressure, the liquid penetrates the micro-crack. The SAC molecules are torn off from the meniscus covering the internal surface of the crack. On the other hand, at the crack orifice, a thin layer of liquid generates additional expansive pressure P_o which is a measure of body *hydro-fillability* (Fig. 1). Pressure P_o is usually lower than pressure P_b because the liquid solvate layer does not penetrate the crack.
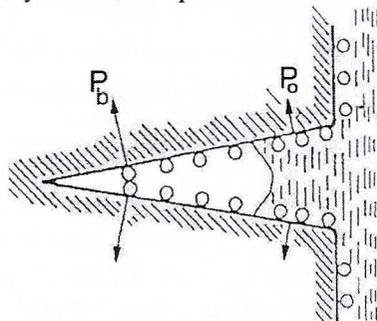

Fig. 1. Scheme of SAC adsorption on the microcrack surface (Percov et al. 1970)

Rys. 1. Schemat adsorpcji ZPC na powierzchni mikroszczeliny

As it can be seen from the above analysis, structural defects are particularly significant for SAC adsorption. Since the structure defects possess additional free energy, the SAC will be adsorbed into them. This explains why the adsorptive decrease of the particle strength is proportional to the frequency of defects on the particle surface. An adsorptive decrease of strength does not occur unless defects are present. Due to the critical influence of the surface defects upon the adsorptive decrease of the particle strength, the same SAC, in identical external conditions, may be greater or less, depending on the physical state of the sample itself. The SAC action is also conducive to the increase in the number of surface cracks. Surface defects, such as dislocations, which do not form active micro-cracks without SAC, develop into micro-cracks in the presence of these compounds. This is due to the fact that the number of dislocations necessary to form a micro-crack, is proportional to the surface energy. The number of dislocations, necessary to form a micro-crack, decreases as the surface energy is lowered. Accordingly, with the same number of dislocations, more active micro-cracks are formed after SAC adsorption. Moreover, the lowering of surface energy facilitates the appearance of dislocations on the solid surface (Rebinder et al. 1956). The probability of forming an active micro-crack can be expressed by a formula (Chodakov 1972):

$$W = C \exp\left(\frac{\gamma a^2}{kT}\right) \tag{6}$$

where:

$$C = \exp\left(\frac{\beta \sigma a^3}{kT}\right),$$

γ — surface tension on phase boundaries,

a — distance between defects,

σ — tensile stress,

k — Boltzmann's constant,

T — temperature,

β — a numerical coefficient ($\beta > 0$).

Therefore, a decrease of surface tension on the phase boundaries, when other factors are determined, increases the probability of forming an active crack.

As has been stated earlier, the process of coagulation of particles of the crushed product occurs simultaneously with the process of comminution. Hence the process of grinding always leads to an equilibrium distribution of the particle size of the product of crushing, i.e. the prolongation of this process does not result in further comminution.

The process of de-aggregation also requires an outlay of energy. The operation of aggregation is expressed by formula (3) or (4), depending on the medium in which the process of grinding occurs. De-aggregation is more intensive when it is carried out in the presence of SAC which, being absorbed on the particle surfaces, tends to block adhesion interactions and simultaneously weakens their susceptibility to coagulation. A similar effect is reached during wet grinding. Since the specific free energy of the solid in relation to the liquid is always smaller than in relation to the gaseous phase, the increase of the solid surface when in liquid requires lower outlays of energy. Greater particle-size reduction is obtained for the same amount of energy input to the system. Nevertheless, if insufficient liquid is added during wet grinding, then liquid bridges are formed between neighbouring particles as a result of the action of capillary forces.

Many authors have investigated Rebinder's effect (Wenstrem 1952; Petrys 1962; Grzymek et al. 1969; Polferov et al. 1971; Ryncarz and Laskowski 1973; Shulze 1992). In all the cases the effect of decrease of tensile strength of particles after SAC treatment was measured in terms of the ratio of the yield of the finest particles. On the other hand, the change in particle-strength as such, under the influence of SAC, was not measured. This paper presents for the first time the results of investigations concerning the effect of SAC on the tensile strength of brittle materials such as limestone and porphyry particles.

3. Experimental procedure

The investigations were performed on particles of two rock types: limestone from Czatkowice and porphyry from Zalas. These materials were selected because limestone is essentially a rock made up of a single mineral substance; calcite (Bolewski 1963) while several mineral phases are included in the Zalas porphyry (Rozen 1909; according to Bolewski 1963), such as albite — 33.5%, anorthite — 9.0%, quartz — 27.5%, potassium feldspar — 14.5%, biotite — 13.0%, apatite — 1.5% and haematite — 1.0%. The strength properties of mono-mineral rocks are only dependant on geometric structural discon-

tinuities, that is, all types of microcracks in the same mineral phase. On the other hand, in rocks more complex in structure, there are discontinuities of physical properties on the boundaries of the different mineral fields (despite geometric discontinuities). The SAC adsorption rate in micro-cracks occurring at field boundaries may be different from that in the micro-cracks contained within a given field. Therefore the rate of change of strength properties under the influence of SAC action may differ for each rock type.

Four samples from both a narrow grain-size range of limestone (25–30 mm) and porphyry grains of 20–30 mm were selected at random. Each sample was made up of 100 particles. Flat and elongated particles were rejected. Single particles from each sample were compressed till the particle began to be·crushed. In every case the value of the breaking force at which the particle collapsed was recorded.

The first 100-particle sample was compressed without prior SAC treatment. The next three samples of limestone and porphyry were immersed for 24 hrs before compression, respectively, in distilled water, a 0.5% aqueous solution of sodium oleate (oleate) and 0.5% aqueous solution of dodecyloamine hydrochloride (amine).

The full range of breaking-point values for each individual sample was divided into several narrow sub-groups according to force values. For each group the yield of particles was measured as well as the value of the breaking stress. The results of these measurements were used to calculate the tensile strength of the particles, the average value of this strength, and to draw a distribution diagram of tensile strengths.

The wetting angles of limestone and porphyry for the above-mentioned SAC solutions were measured to evaluate the free surface energy on which the tensile strength of particles depends. Five sections of limestone and five of porphyry were prepared. Measurements of the wetting angle by means of the settled drop method were performed on these sections. The procedure was undertaken in the Institute of Catalysis and Surface Physico-chemistry of the Polish Academy of Science in Cracow.

4. Results and discussion

The value of the tensile strength of the particles was calculated from the following formula (Brożek 1996):

$$\sigma = 0.74\,\frac{P}{D^2}\quad\text{(for limestone)} \tag{7a}$$

$$\sigma = 0.71\,\frac{P}{D^2}\quad\text{(for porphyry)} \tag{7b}$$

where:

  P — value of breaking force,

  D — mesh diameter of a particle, whilst the numerical coefficients were determined experimentally (Brożek 1996).

Fig. 2–9 present the distribution functions of particle tensile stress in the system of variables $\left(\dfrac{\sigma}{\overline{\sigma}}, P_r\right)$. The distribution function of the particle strength is expressed by Weibull's distribution (Weibull 1951):

$$P_r = 1 - \exp[-c(\sigma/\overline{\sigma})^m] \tag{8}$$

where:

    m — Weibull's modulus,

    c — a constant connected with Weibull's modulus by the gamma function

$$c = \Gamma^m\left(1 + \frac{1}{m}\right)$$

The value of Weibull's modulus was calculated experimentally by fitting dependence (8) to the experimental data. The quality factor of fit was measured by the following index given by Doremus (Doremus 1983):

$$Q = \frac{\sum_{i=1}^{n}(x_i - \hat{x}_i)^2}{\sum_{i=1}^{n}(x_i - 1)^2} \qquad x = \frac{\sigma}{\overline{\sigma}} \tag{9}$$

where $\hat{x}_i$ is a relative value of strength, obtained from the condition $\hat{P}_r(\hat{x}_i) = P_r(x_i)$. Accordingly, the value $\hat{x}_i$ was calculated from the following equation:

$$\hat{x}_i = \left[-\frac{1}{c}\ln(1 - P_r)\right]^{1/m} \tag{10}$$

For $Q = 1$ the fit is ideal. Practically, for $Q > 0.95$ the fit is good while for $Q < 0.9$ the fit is unsatisfactory.

The detailed formulae of strength distributions and Q indexes, obtained by means of the least-square method, are as follows:

a) untreated limestone particles

$$P_r = 1 - \exp[-0.73\,(\sigma/\overline{\sigma})^{3.42}] \tag{11}$$

$$Q = 0.947$$

b) limestone particles after treatment with distilled water

$$P_r = 1 - \exp[-0.9\,(\sigma/\overline{\sigma})^{3.21}] \tag{12}$$

$$Q = 0.962$$

c) limestone particles after treatment with sodium oleate solution

$$P_r = 1 - \exp[-0.91\,(\sigma/\overline{\sigma})^{3.0}] \tag{13}$$

$$Q = 0.985$$

d) limestone particles after treatment with amine solution

$$P_r = 1 - \exp[-0.76\,(\sigma/\overline{\sigma})^{2.65}] \tag{14}$$

$$Q = 0.982$$

e) untreated porphyry particles

$$P_r = 1 - \exp[-0.84\,(\sigma/\overline{\sigma})^{3.47}] \tag{15}$$

$$Q = 0.941$$

f) porphyry particles after treatment with distilled water

$$P_r = 1 - \exp[-0.93\,(\sigma/\overline{\sigma})^{2.57}] \tag{16}$$

$$Q = 0.987$$

g) porphyry particles after treatment with sodium oleate solution

$$P_r = 1 - \exp[-0.89\,(\sigma/\overline{\sigma})^{2.81}] \tag{17}$$

$$Q = 0.989$$

h) porphyry particles after treatment with amine solution

$$P_r = 1 - \exp[-0.91\,(\sigma/\overline{\sigma})^{2.81}] \tag{18}$$

$$Q = 0.984$$

Dependences (11)–(18) are marked with a continuous line in Fig. 2–9. Taking into account the value of the Q index, Weibull's distribution approximates well to the tensile strength distribution of irregular mineral particles and the calculated values of Weibull's modulus can be considered reliable.

Table 1 shows the relationship between the values of Weibull's modulus m, the average values of particle strength of the tested samples $\overline{\sigma}$ and average percentage decrease of particle strength after SAC treatment $\Delta\sigma/8.3$ and $\Delta\sigma/7.58$ for limestone and porphyry respectively.

As it is shown in Table 1, after treatment with distilled water, the average tensile strength of limestone particles decreased by 4.46% as compared to the average strength of untreated particles. The comparable lowering of strength after treatment with the oleate solution is 13.73% for limestone and 21.93% after treatment with the amine solution. Thus water exerted a only a slight influence upon the lowering of strength in the case of limestone. Only after the application of SAC did the decrease of strength become significant.
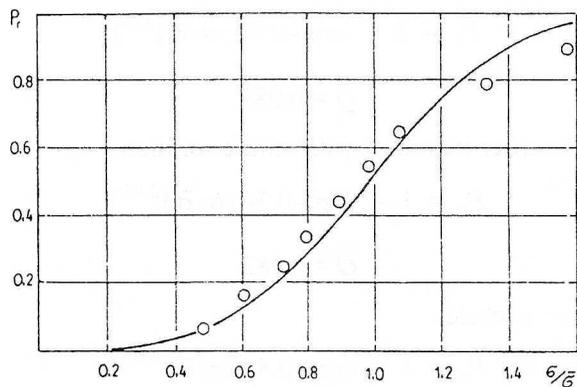
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Fig. 2. Distribution of strength of limestone particles without treatment

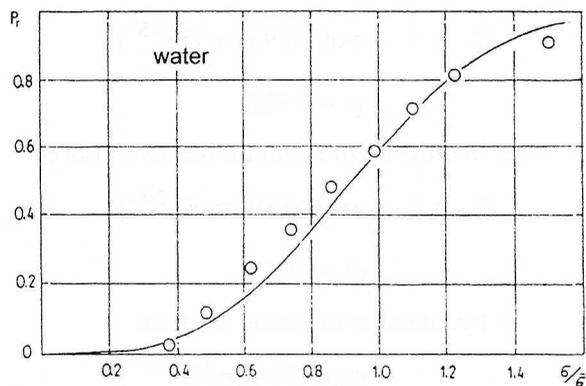Rys. 2. Rozkład wytrzymałości ziaren wapienia bez obróbki

Fig. 3. Distribution of strength of limestone particles after treatment with distilled water

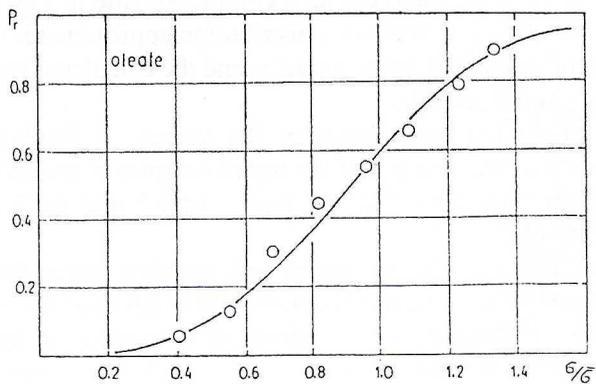Rys. 3. Rozkład wytrzymałości ziaren wapienia po obróbce wodą destylowaną

Fig. 4. Distribution of strength of limestone particles after treatment with oleate solution

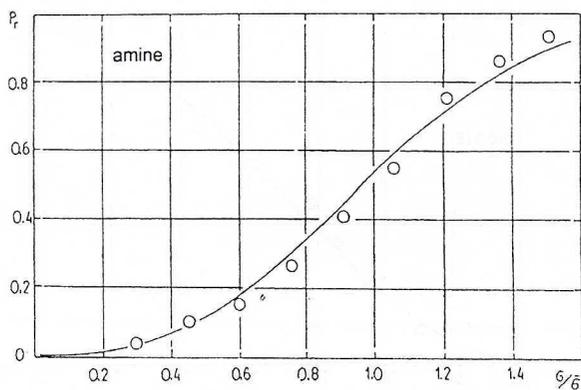Rys. 4. Rozkład wytrzymałości ziaren wapienia po obróbce roztworem oleinianu

Fig. 5. Distribution of strength of limestone particles after treatment with amine solution

Rys. 5. Rozkład wytrzymałości ziaren wapienia po obróbce roztworem aminy
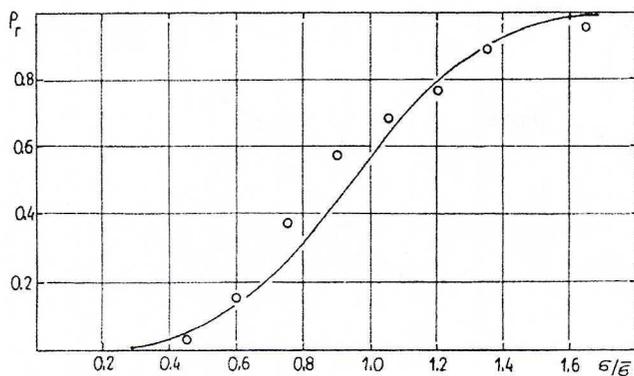

Fig. 6. Distribution of strength of porphyry particles without treatment

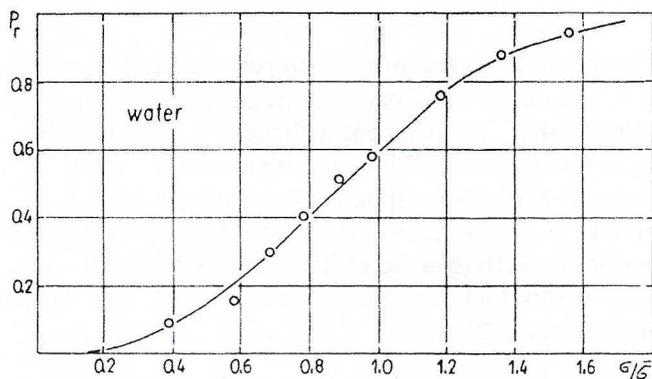Rys. 6. Rozkład wytrzymałości ziaren profiru bez obróbki

Fig. 7. Distribution of strength of porphyry particles after treatment with distilled water

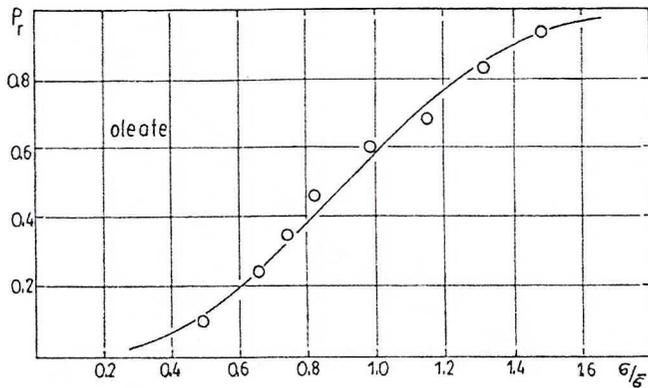Rys. 7. Rozkład wytrzymałości ziaren profiru po obróbce wodą destylowaną

Fig. 8. Distribution of strength of porphyry particles after treatment with oleate solution

Rys. 8. Rozkład wytrzymałości ziaren profiru po obróbce roztworem oleinianu
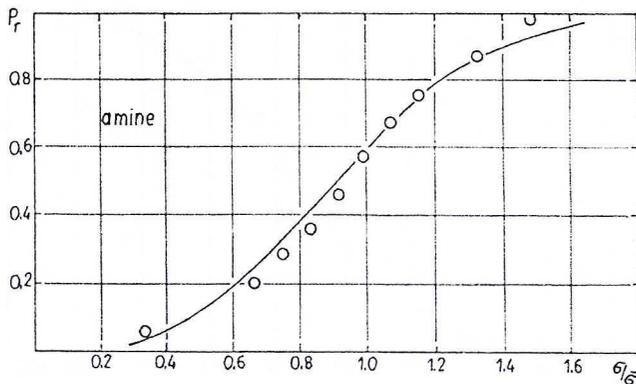

Fig. 9. Distribution of strength of porphyry particles after treatment with amine solution

Rys. 9. Rozkład wytrzymałości ziaren profiru po obróbce roztworem aminy

In the case of porphyry the effect of SAC on particle strength is lower. As it can be seen from Table 1, the decrease of particle strength after treatment with the oleate solution was 8.7% and 9.4% after treatment with the amine solution. By comparison, the decrease of strength was more than 23% after treatment with distilled water.

The difference in the SAC effect upon the limestone and porphyry particles can be explained by applying the results of measurements of the wetting angle. Table 2 presents the average values of the wetting angle of limestone and porphyry after 1 minute.

The free surface energy (surface tension) is connected with the wetting angle by Young's equation (Drzymała 2001):

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos\theta \qquad (19)$$

where:

γ_{SL} — surface tension on the solid-liquid boundary,

γ_{SV} — surface tension on the solid — air boundary,
γ_{LV} — surface tension on the liquid — air boundary,
θ — wetting angle.

As it results from formula (19), $\gamma_{SL} < \gamma_{SV}$ and with the increase of the wetting angle θ the surface tension (surface energy) grows on the solid/liquid phase-boundaries.

Taking into account the differences in the values of the wetting angle (with water) for limestone and porphyry, water should exert a much stronger effect on the decrease of strength of porphyry than in the case of limestone.

As it is indicated by the results of strength tests of Table 1, the strength of untreated limestone particles is higher than for untreated porphyry. This implies that there are more active cracks in porphyry than in limestone. After activation with distilled water, the limestone surface reveals higher surface tension than the porphyry, which is confirmed by the significantly larger wetting angle on limestone (78°) than on porphyry

TABLE 1

Average strength and values of Weibull's modulus of the tested samples

TABLICA 1

Wytrzymałość średnia oraz wartości modułu Weibulla badanych próbek

Sample		Without treatment	Water treatment	Treatment with oleate	Treatment with amine
Limestone	$\bar{\sigma}$ [MPa]	8.30	7.93	7.16	6.48
	m	3.42	3.21	3.00	2.65
	$\Delta\bar{\sigma}/8.3$	0%	4.46%	13.76%	21.93%
Porphyry	[MPa]	7.58	5.81	6.92	6.87
	m	3.47	2.57	2.81	2.81
	$\Delta\bar{\sigma}/7.58$	0%	23.31%	8.69%	9.34%

TABLE 2

Average wetting angles of limestone and porphyry $\theta[°]$ (after 1 minute)

TABLICA 2

Średnie kąty zwilżania wapienia i profiru $\theta[°]$ (po 1 minucie)

	Limestone	Porphyry
Water	78	52
Oleate solution	48	42
Amine solution	18	31

(52°). Consequently, after treatment with distilled water, the strength of the limestone particles is much higher than for porphyry. The higher strength of the limestone particles, according to formula (6), results from the smaller probability of generating an active micro-crack due to higher surface tension and a smaller number of primary micro-cracks which are penetrated by water under the influence of capillary forces. This is due to the more pronounced effect of distilled water on lowering the strength of porphyry as compared to limestone. In case of some solids, water decreases their strength most strongly (Ryncarz and Laskowski,1973). In case of the amine solution the porphyry surface reveals a larger wetting angle (31°) than the limestone surface (18°). Therefore the strength of porphyry particles after treating them with the amine solution is higher than the strength of limestone particles. A significant decrease in the strength of limestone particles treated with the amine solution in relation to the strength after treatment with water may be explained by the higher decrease of surface tension. This is proved by the significantly lower value of the wetting angle after treatment with the amine solution (18°) as opposed to the value of the wetting angle after treatment with water (78°).

5. Final remarks

As the investigation results indicate, the distribution of the strength of mineral particles is compatible with Weibull's distribution. The compatibility index of the empirical distribution with the model distribution is very high ($Q > 0.94$). Both for limestone and porphyry the applied surface-active compounds reduce the particle strength. On the other hand, the degree of reduction of tensile strength by means of the same compound differs. In case of limestone, which is a homogeneous material, the greatest strength-reduction is obtained after treatment with the amine solution whereas in case of porphyry (which is a heterogeneous material) the same decrease was observed after treatment with distilled water. This differentiation of the decrease of strength of limestone and porphyry particles and treatment with the same compounds can be confirmed by the values of the wetting angle of each material when subjected to the same surface active compound (according to Young's and Griffith's formulas, a larger wetting angle indicates on a higher particle strength). The wetting angle depends on the type of compound applied. The strength of limestone particles is shown by an increase of the wetting angle. Therefore the effect of SAC upon the decrease of strength of homogeneous materials can be estimated by measuring of the wetting angle. In case of heterogeneous materials the value of the angle of wetting with various compounds does not necessarily correlate with the values of average particle-strength, since the action of SAC depends to a large extent on the mineral composition of a given material. This results from the fact that the mechanism of the SAC action and the degree of adsorption in the cracks at the boundaries of mineral phases can depend on the type of minerals conjoined. It would seem desirable that these hypotheses be confirmed by testing other homo- and heterogeneous materials. Investigations on the effect of SAC on the strength

of mineral particles should be continued. Despite water alone strongly decreasing the strength of some solids, further investigation into the influence of SAC concentrations upon the decrease of particle strengths of other minerals and other SAC might yield useful information.

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