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Film Influence on Mineral Surface Properties in Flotation Aspects

Badania wpływu filmów na własności powierzchniowe minerałów w aspekcie ich flotowalności

Исследования влиянии фильмов на поверхностные свойства минералов в аспекте их флотации

To utilize the mineral ores that occur in nature they require to be allowed for the enrichment processes. The proper choice of the method, among others, depends upon the physico-chemical properties of the mineral and gangue. As yet, one of the principle methods for the enrichment is the flotation. But in the last few years works were done in which other physico-chemical phenomenona have been accounted for selective aggregation of the mineral particles and next, their isolation from the suspension. The following methods can be mentioned here: shear flocculation [1-3], aggregation flotation [4-7] and spheric agglomeration [8-10]. In all the methods the basic matter are the energetic changes at the solid - liquid, solid - gas and liquid - gas interfaces [11], which result from polar and dispersion interactions. Interaction of the chemical compounds, that are used with the solid surface, depends upon the nature of the compound and the nature of the solid surface. The surface of the solid is a hydrophobic one if under its creation the ionic or covalent bonds are not broken. However, even in case of the hydrophobic surface nonpolar collectors are used to improve beneficiation of the mineral. These collectors act with the surface by dispersion forces only. Nonpolar compounds film on the mineral surface decreases its surface free energy and transforms it to the hydrocarbon surface. In effect, it lowers the thickness and the stability of the water film at the surface and makes easier adhesion of air bubbles to mineral particles, as a result of energetic barrier decrease.

In this paper the results of studies of nonpolar film properties (n-alkanes) on the sulfur surface are discussed. The paper is a summary of the studies conducted on this subject in the last few years in the Flotation Laboratory, Department of Physical Chemistry UMCS, at the head of Prof. Andrzej Waksmundzki.

PROPERTIES OF N-ALKANES FILM IN SULFUR/FILM - WATER SYSTEM

The formation of a hydrocarbon film on the sulfur surface effects the energy changes. The magnitude of these changes depends upon the amount and kind of n-alkane [13-15]. Properties of the films, in homologous series from hexane to hexadecane, were tested throughout measurements of the contact angle [14], adhesion forces of air bubble to sulfur surface wetted with the alkanes, zeta potential of this surface in water [15, 17], and water vapour adsorption on the sulfur surface wetted with n-alkanes [18]. The practical aspect of the studies were the flotation tests of sulfur in the presence of the alkanes or diesel oil [4,5,16,19].

Energy changes of the solid surface (sulfur) continue until the outermost layer of the film reaches the value of the surface tension of hydrocarbon [14]. However, n-alkane film thickness could be greater than that, resulting from the extent of the surface forces of the solid. For instance, the film thickness, after wetting (immersion) the sulfur surface with hydrocarbon, is greater than it could be expected from the maximum decrement of its surface free energy. If the air bubble is contacted with the film then a part of the alkane spreads on the bubble surface and, after bubble removing, the film becomes thinner. Such a process takes place for every following contacted air bubble, until the film reaches the energy higher than energy of spreading at the water-air interface. It corresponds to some "limiting thickness" of the film that is characteristic of each of the tested hydrocarbons. This thickness will be greater for higher than shorter chain-length of hydrocarbons [14,16]. It results from:

1) positive value of the spreading coefficient for hexane, heptane and octane on water, and negative value of that for n-alkanes further in series;

2) adsorption from the air bubble of n-alkane vapour at water - vapour interface;

3) magnitude of the interactions resulting from surface tension of the hydrocarbon.

Therefore, for hydrocarbons having a smaller number of carbon atoms establishment of the adhesion forces and the contact angle which results from here , will occur for the smaller number of attachment - detachment acts of the air bubbles. An illustration of the results are the changes of the parameters with chain length presented in Fig. 1 [14,16], e.g. for hexadecane (curve 1 and 1'), pentadecane (curve 2 and 2'), hexane curve (3 and 3') and heptane (curve 4 and 4'). It is seen that, initially, adhesion forces increase for each successively contacted air bubble, whereas the contact angle values decrease and both of the parameters tend to reach constant values. The contact angle and adhesion forces values clearly depend on the film thickness and chain length of the alkane.

Changes in n-alkane film thickness, and hence resulting the energetic changes are reflected also in zeta potential of sulfur [16,17] and water adsorption on it [20]. These results are presented in Fig. 2, where zeta potential (mV) and amounts of adsorbed water (mmol/g) are shown as a function of number of statistical monolayers of n-heptane at 20°C. Both of the parameters decrease with the increasing coverage of the sulfur surface by n-heptane. But in case of water adsorption, a minimum appears at the first monolayer of heptane and a slight maximum at the second monolayer of it. The vertical

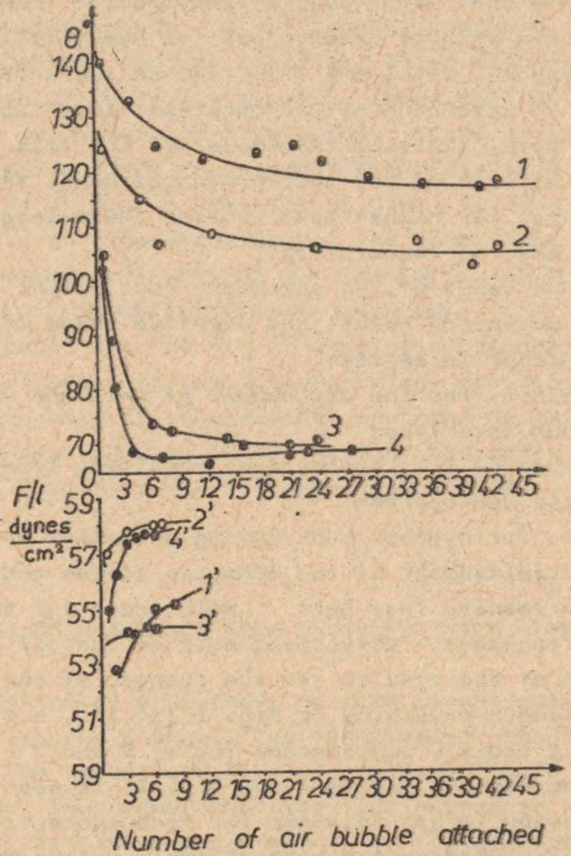

Fig. 1. Changes of contact angle (θ) and stability (F/l) of the sulfur/film - air bubble - water system as a function of number of air bubbles adhered to the sulfur surface wetted with n-alkane; 1, 1' - hexadecane, 2, 2' - pentadecane, 3, 3' - hexane, 4, 4' - heptane

orientation of heptane molecules ($18\ \text{Å}^2$ of cross-section) on the sulfur surface has been assumed here. Such an orientation results from calculations [15] based on Fowkes's theory [21], and also from adsorption isotherms determined on sulfur for heptane, octane and nonane [22].

Results presented in Fig. 2 show that up to 3 statistical monolayers of heptane, both zeta potential and water adsorption changes go nonmonotonously. It suggests that in this range of the sulfur surface coverage the greatest changes of the heptane

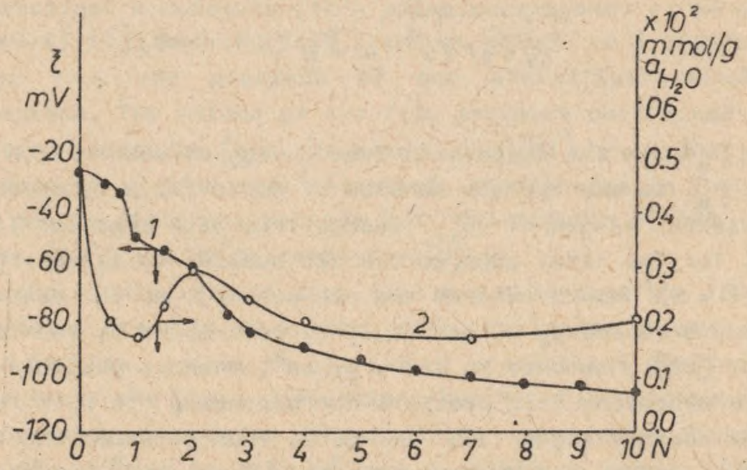

Fig. 2. 1 - changes of zeta potential (ζ), 2 - water adsorption (a) as a function of number of statistical monolayers

film structure take place, at the cost of changes of the surface free energy of sulfur. At higher coverages the energetic changes are small, which appears in small and monotonous changes of the discussed parameters. Therefore, in reality, it is difficult to say that n-heptane molecules are vertically oriented at the higher coverage of the surface. The amounts of adsorbed water on the bare sulfur surface (Fig. 2) correspond to 4.5 of statistical monolayers, whereas for the monolayer of n-heptane film the adsorption decreases to ca 1.3 of water monolayers. This fact is obvious in view of the sulfur free energy decrement caused by n-heptane and resulting from the drop of interactions at sulfur/film - water interface. It also reflects on sulfur/film - air bubble in water system stability and hence contact angle values [13,14]. Comparing the results from Fig. 1 with those of Fig. 2, it may be stated that thinning the n-heptane film by adhered and removed in series the air bubbles leads to a stable film, having 1-3 statistical monolayers of thickness. This results from the following considerations. Taking into account the changes of the contact angle (Fig. 1), which for n-heptane ranged from 105° to 68°, free energy changes of sulfur surface covered by the film may be calculated from Young equation.

$$2\sqrt{\gamma_{sf}\gamma_w^d} = \gamma_w\,(1 + \cos\theta) \qquad (1)$$

where γ_w^d is the dispersion free energy of water (21.8 dynes/cm), γ_w is the surface tension of water (72.8 dynes/cm). Calculated values of γ_{sf} change from 33.4 ergs/cm^2 (for θ = 105°C for the first adhered the air bubble) to 114.8 ergs/cm^2 for θ = 68° ninth adhered the air bubble). As the value of the surface free energy of bare sulfur, determined by two-liquid method [23], amounts to 124 ergs/cm^2, then is possible to calculate n-heptane film pressure corresponding to both values of the contact angle (105° and 68°). Thus obtained the film pressure values are 90.6 ergs/cm^2 and 9 ergs/cm^2, respectively. These values may be compared with the film pressure determined from the electrokinetic measurements [15,17].

In Fig. 3 the film pressure values are shown as a function of number of statistical monolayers of n-heptane, determined from zeta potentional measurements (curve 2) [15] and for comparison - from adsorption measurements (curve 1) [22]. The film

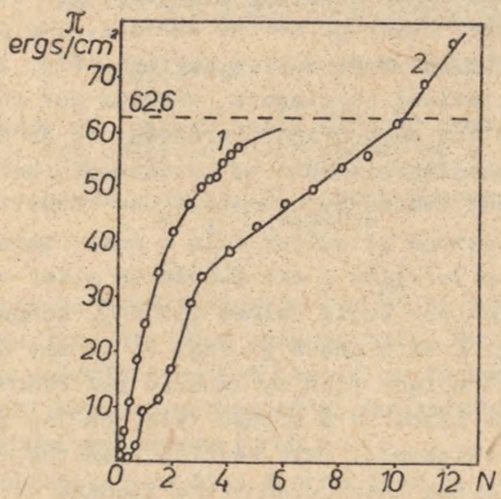

Fig. 3. Film pressure(π) of n-heptane on sulfur against number of statistical monolayers; 1 - values determined from adsorption isotherms, 2 - values determined from electrokinetic measurements

pressure equal to 90.6 ergs/cm^2 (Fig. 3, curve 2), lies above 12 statistical monolayers (this value corresponds to 14 of the monolayers) [15], and the film pressure equal to 9 ergs/cm^2, results from the presence of one statistical monolayer of n-heptane. The values of the film pressure determined from adsorption isotherms (gas chromatography) [22] are higher than those determined from zeta potential. Differences in the values may be due to different methods and temperatures of the measurements (30°C and 20°C, respectively).

The above calculations show that for n-heptane the limiting thickness of its film on sulfur, which could not be removed by the air bubbles, amounts to ca. 1-3 of statistical monolayers. This confirms the above discussion that at this thickness the film possesses an ordered structure. For increasing chain length of n-alkane it will be less possible to remove the hydrocarbon thick film from the sulfur surface by the air bubbles. For instance, in case of hexadecane (Fig. 1) the established value of θ equals to 117° and it corresponds to 18.1. ergs/cm^2 of the free energy of sulfur covered with the film. Therefore, the film pressure amounts to 105.9 ergs/cm^2. Thus it shows that energy of the outermost layer of the film is close to the surface tension value of hexadecane. It ought to be pointed out that melting temperature of hexadecane is 20°C (that is, it equals to the temperature of the measurements [14]). Therefore, the possibility of removing the film by the air bubbles is smaller and the limiting thickness of n-alkane film is connected closely with the chain length. The same is true with respect to the changes of zeta potential of sulfur wetted with n-alkane [17], contact angle [14], adhesion forces of the air bubble [16], water adsorption on the sulfur surface [20], and also flotation activity of sulfur [13, 14, 16, 19].

An illustration of this is Fig. 4, where the differences in values of the proper parameters obtained for each subsequent and antecedent alkane in the tested series, are shown as a function of number of carbon atoms in the chain of antecedent alkane. In the same way there are also shown the differences in melting temperature of the alkanes $\Delta T_m = T_m(C_n) - T_m(C_n - 1)$. All the differences change in a "jumping" way. This leads to the conclusion that n-alkanes film structure on sulfur is similar to that

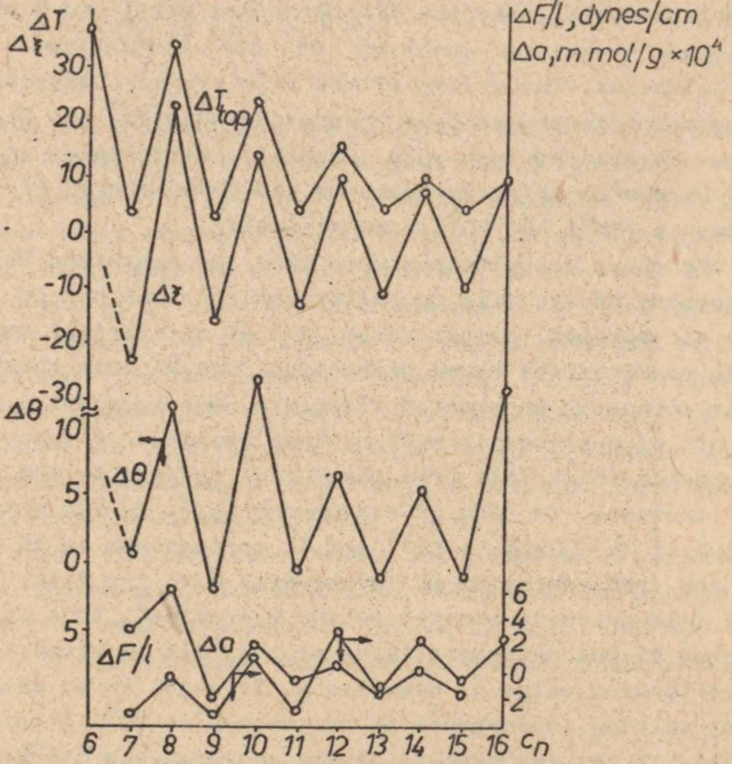

Fig. 4. Differences in zeta potential (Δζ), contact angles (Δθ), water adsorption (Δa) and adhesion forces (ΔF/l) for sulfur wetted with n-alkanes and differences in metting temperatures of the alkanes, as obtained by substraction the value of the parameters for chain langth C_{n-1} from the value for C_n; the differences shown against chain length, C_n, of n-alkane

for solid state of the alkanes, as the measured parameters result from energetic changes in the film. The surface tension of the alkanes at 20°C changes monotonously with chain length, but near their melting temperature it changes in a "jumping" way, from alkane to alkene [14], and hence the above conclusion.

ENERGETIC CHANGES IN SULFUR/FILM - WATER SYSTEM IN RELATION TO FLOTABILITY OF SULFUR

In flotation process the amount of hydrocarbon emulsion, used as a nonpolar collector (ca. 400 g/t), usually does not overrun the amount necesarry to cover the sulfur surface with a monolayer [24]. Therefore, the adhesion forces and the contact angle values presented in Fig. 1 concern a higher thickness of n-alkane film, and only the established values from Fig. 1 are relative to the flotation conditions. Then it may be concluded that flotability of sulfur depending on chain length of n-alkane would change in similar way as the parameters shown in Fig.4. In order to show this in Fig.5 there is drawn the dependence of content of sulfur in concentrates relative to the chain length of hydrocarbon used for flotation. Curve 1 concerns natural sulfur ore flotation and curve 2 - flotation of feed obtained by mixing sulfur with marble. In both cases the content of sulfur in the feed was 26.3%. The froth flotation tests were carried out in a laboratory flotation machine at consumption of 400 g of n-alkane (as a collector) and 200 g of pine oil (as a frother) per ton of the feed [16,19].

In Fig. 5 (curve 3) there are also drawn results of pure sulfur flotation in Hallimond tube, in the form of nitrogen volumes needed for floating 100% of the samples wetted with n-alkane against its chain length. Dry surface of the sulfur samples was wetted in series with 1 μl of n-alkane per 1.5 g of the sample. In all three cases (Fig. 5) a good correlation of the changes in flotability can be seen. The changes go in similar way as those for parameters presented in Fig. 4. It confirms again the above conclusion concerning structure and stability of n-alkane film on the sulfur surface. However, it must be taken into account that the sulfur ore is composed, on the average, of 25% of sulfur and 75% of gangue, where limestone is the main component., Moreover, the sulfur ore is in contact with bed water, which contains a considerable amount of sulfides. The sulfide ions, first of all, modify the surface of limestone [25,26]. The frother agents, which are used in froth

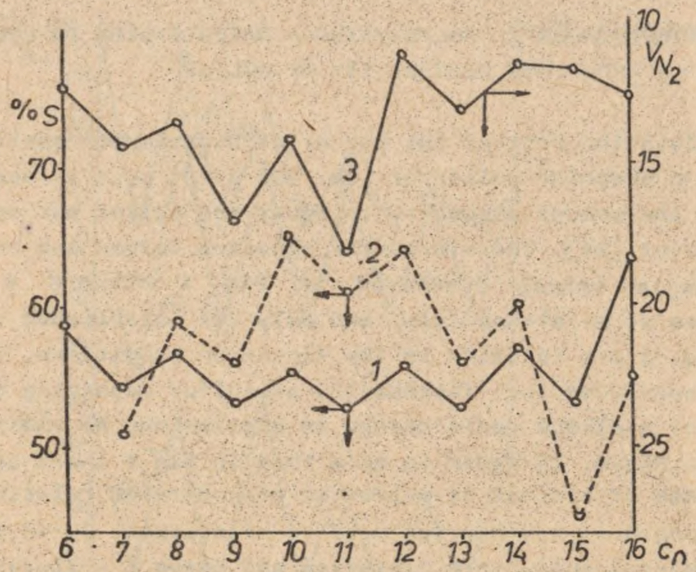

Fig. 5. Influence of chain length of n-alkane on the sulfur content in concentrates; 1 - flotation of sulfur are from Tarnobrzeg, 2 - feed obtained by mixing sulfur with marble, 3 - volumes of nitrogen consumed for floating completely the same sulfur samples wetted with n-alkane in Hallimond tube as a function of the chain length

flotation, also modify properties of the hydrocarbon film on the sulfur surface [4,5].

Various factors, acting in the flotation process and kinetic conditions of the process, cause that changes of the discussed parameters may not be synonymously correlated with flotability of sulfur. The frother agents having polar character, absorb both on the limestone surface and on the sulfur surface. Molecules of the frother agents orient themselves on sulfur with their polar head toward the solution - on the contrary to limestone. In the result the sulfur surface becomes more hydrophilic and that of limestone more hydrophobic. Evidences for this are the results presented in Fig. 6, where changes of adhesion forces of the air bubble to the sulfur surface (curve 1) and to calcite surface (curve 2) are shown in the pine oil solutions, for concentration range 0-200 mg/dcm^3 [27]. As the pine oil concentration increases the adhesion forces to

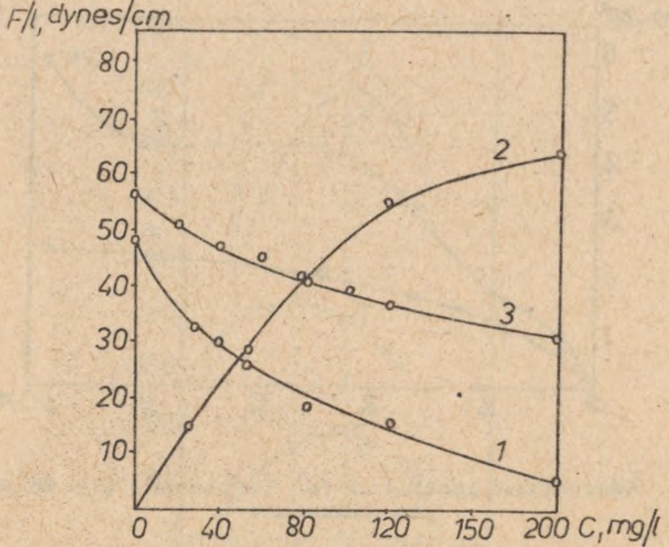

Fig. 6. Influence of pine oil concentration on the stability of 1 - sulfur - air bubble - water system, 2 - calcite - air bubble - water system, 3 - sulfur n-hexane film - air bubble - water system

calcite surface grow from 0 to 65 dynes/cm, whereas those to sulfur surface decrease from ca. 50 dynes/cm to ca. 5 dynes/cm. Fig. 6 (curve 3) shows also the changes of estabilished values for adhesion forces of the air bubble to the sulfur surface wetted with hexane relative to pine oil concentration. Here appears also decrement in stability for sulfur/film - air bubble system although smaller than that for bare sulfur surface, but reaching almost 50% in the studied range of pine oil concentration. A similar shape of the curve of the adhesion forces changes has been stated for calcite and sulfur in α-terpinol solutions. Changes of the parameters (Fig. 6) result from adsorption of polar molecules at the solid - solution and solution - gas interfaces.

Quantities of α-terpinol adsorption on sulfur and marble surfaces are shown in Fig. 7, curves 1 and 2, respectively. The adsorption on the marble surface is about twice higher than on the sulfur surface. Therefore, the adhesion forces of

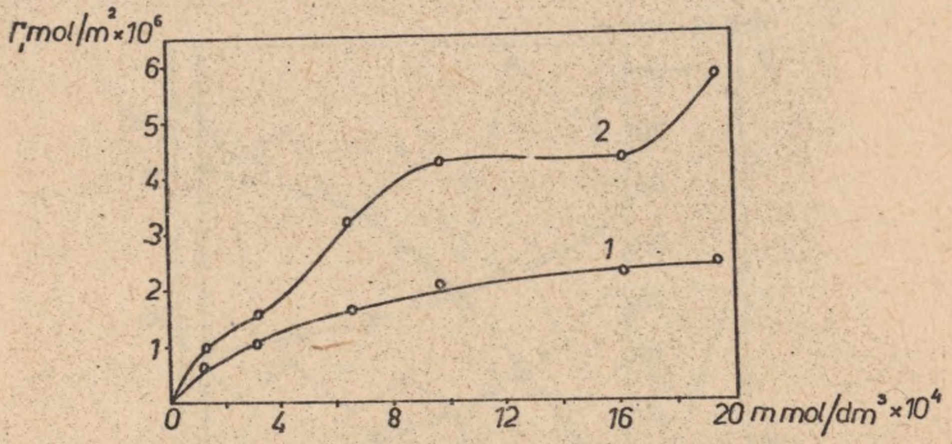

Fig. 7. Adsorption isotherms for terpineol: 1 - on sulfur, 2 - on limestone

the air bubble to the marble surface grow and exceed even those to the sulfur surface wetted with n-hexane (Fig. 6). Results presented in Figs. 6 and 7 clearly show the negative influence of the frother agents in the froth flotation. These agents magnify limestone flotability, the slime particles of which (besides that) are carried out in water film surrounded the air bubble and collector droplets [28].

Figure 8 presents the limestone slimes carrier (for bare surface and for the surface conditioned with sulfide solution) with the air bubbles (curves 1 and 2, respectively) and with n-heptane droplets (curve 1' and 2'), as a function of pH solution. The maximum in recovery appears at pH value corresponding to the point of zero charge of limestone, where the surface acquires the highest hydrophobicity. This value of pH is also equal to the natural pH value of the flotation pulp.

Results presented in Figs. 6, 7 and 8 indicate that frother agents decay effectivity (selectivity) of the froth flotation process. Therefore, an enrichment method was elaborated where the frother agent was eliminated [4,5]. The method is based on, previous to the flotation, conditioning of the pulp by stirring in a suitable container, or, according to the other version ,

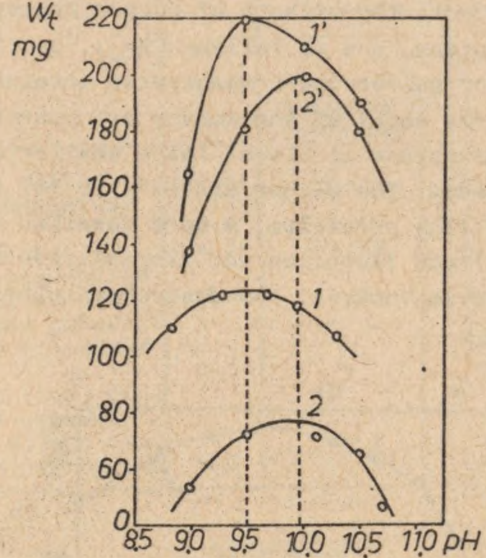

Fig. 8. Dependence of the limestone slimes carrier on pH value of the suspension in presence of Tween 80; 1 and 1´ - for bare limestone, 2 and 2´ - for limestone previously conditioned in sulfide solution, 1 and 2 - carriers on air bubbles, 1´ and 2´ - carries on n-heptane droplets

directly in the flotation machine, without areation. Stirring of the pulp in the presence of diesel oil as a collector, leads to selective aggregation of the sulfur particles. Then, the aggregates are isolated from the pulp by areation and without any addition of the frother agent. It was found out that water glass addition,previously to the collector, essentially improves effectivity of the process [5]. Water glass acts here as a peptiser and probably prevents formation of the aggregates of limestone - limestone and limestone on sulfur particles. This probably provides the formation of "pure" aggregates of sulfur particles and their higher fastness. An additional effect is the decrement in the collector consumption [5].

Figure 9 is an exemplary illustration of the results of the sulfur ore enrichment by the described method for 0,25 kg/t of diesel oil consumption, at various additions of the water glass. The best results were achieved for 3 kg of water glass addition per ton of sulfur ore. The effects of such a process, in comparison to froth flotation, are as follows [24]: for the same in both cases recoveries of sulfur the concentrates obtained by this method are higher by about 8% and wastes are poorer by ca. 1%. The collector consumption is almost twice smaller and frother agents are not needed. The method allows also for selective flotation of very fine particles. A more detailed comparison of the results from froth flotation and flocculation flotation methods are listed in Table 1. The described method has also been patented [29].

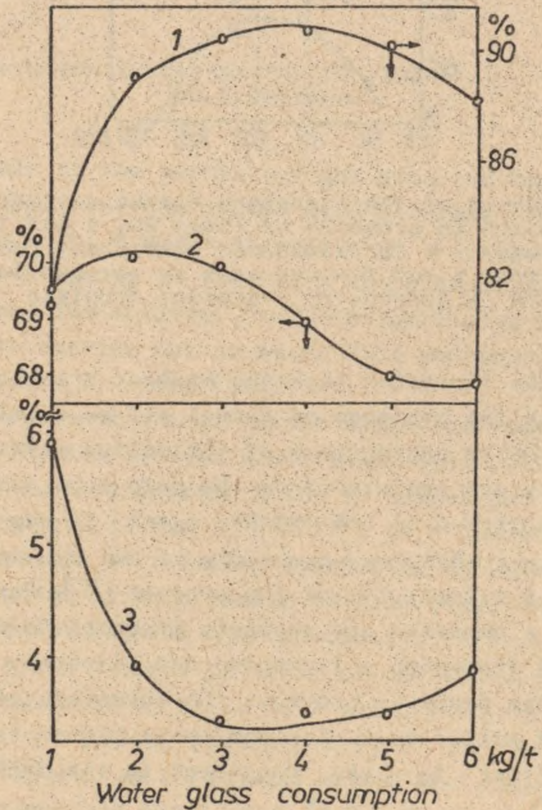

Fig. 9. Water glass influence on sulfur ore benefication at 0.25 kg/t of collector consumption; 1 - recovery of sulfur, 2 - content of sulfur in concentrates, 3 - content of sulfur in wastes

Table 1. Results of sulfur ore enrichment by various methods

Flotation parameters	Froth flotation	Flocculation flotation			
		Feed conditioned in:			
		Suitable container	Flotation machine		
Recovery of sulfur, %	98.8	90.3	89.0	90.0	92.0
Sulfur in concentrates,%	58.0	74.0	66.0	70.0	68.0
Sulfur in wastes,%	4.3	3.75	4.0	3.4	2.9
Collector consumption, kg/t of sulfur ore	0.4	6.0	3.0	0.25	1.0
Frother agent consumption, kg/t of sulfur ore	0.1	-	-	-	-
Time of stirring, min.	4	10	10	10	10
Water glass consumption, kg/t of the ore	-	-	-	3.0	3.0
Size of ore grains, mm	0.3	0.06	0.2	0.2	0.2

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STRESZCZENIE

Wzbogacenie minerałów z natury hydrofobowych, mimo ich własności, wymaga stosowania odczynników zbierających i pianotwórczych, które modyfikują własności powierzchniowe tych minerałów. Przedstawiono wyniki badań nad wpływem odczynników flotacyjnych na zmiany takich wielkości fizykochemicznych, jak: kąt zwilżania, siłę sczepienia ziarno-pęcherzyk, siłę zlepienia ziarno-ziarno i zmiany potencjału elektrokinetycznego. Ponadto przeprowadzono badania wpływu filmów substancji apolarnych na wielkość adsorpcji pary wodnej oraz wynoszenie skały płonnej w otoczkach wodnych pęcherzyków gazu i kropelek cieczy apolarnej. Na podstawie uzyskanych wyników wyprowadzono wnioski dotyczące wpływu tych odczynników na efektywność procesu wzbogacania. Wyniki te pozwoliły również opracować bardziej efektywny sposób wzbogacania tego typu minerałów.

Резюме

Обогащение гидрофобных минералов требует использования собирателей и пенообразующих средств, которые влияют на поверхностные свойства этих минералов. В данной работе показаны результаты исследований влияния флотационных реагентов на изменение физико-химических параметров как: угол смачивания, силы прилипания зерно-пузырёк, силы прилипания зерно-зерно и изменения электрокинетического потенциала. Кроме того проведено исследования влияния фильмов аполярных веществ на величину адсорпции водного пара, а также на извлечение шламов в водяных оболочках пузырьков воздуха и капельках аполярной жидкости.

На основании полученных результатов выведено предложения касающиеся влияния этих реагентов на эффекты процесса обогащения. Эти результаты позволили также разработать более эффективный метод обогащения минералов такого типа.