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## OIL AGGLOMERATION OF MINERAL TAILINGS IN MIXED-SURFACTANT SYSTEMS

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### AGLOMERACJA OLEJOWA ODPADÓW MINERALNYCH W OBECNOŚCI MIESZANINY SURFAKTANTÓW

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#### Abstract

In this paper the results of spherical oil agglomeration of mineral tailings were presented. Tailings from nickel recovery (the Szklary heap, Lower Silesia, Poland) were used in these investigations. Agglomeration experiments have been carried out in water suspension of mineral particles in the presence of cationic and anionic surfactants and kerosene as bridging oil.

*Keywords: oil agglomeration, mineral tailing, ionic surfactants*

#### Streszczenie

W niniejszym artykule przedstawiono wyniki badań procesu aglomeracji olejowej odpadów mineralnych, pozostałych po hutniczej obróbce rudy niklowej, zgromadzonych na hałdzie w okolicach miejscowości Szklary na Dolnym Śląsku. Proces prowadzono w zawiesinie wodnej cząstek mineralnych w obecności surfaktantu kationowego oraz anionowego, użytych jako substancje modyfikujące właściwości powierzchniowe ciała stałego oraz emulgatora oleju (nafty) w wodzie.

*Słowa kluczowe: aglomeracja olejowa, odpady mineralne, surfaktanty jonowe*

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## 1. Introduction

Spherical oil agglomeration is a process commonly used to recover or separate fine particles dispersed in water through the addition of oil; the name of the technique is due to the final shape of the agglomerates [1]. This technique has been used in the mineral industry since the 1920s for the purification of coal from sulphur and ashes. Other applications of the spherical agglomeration include the recovery of valuable particles from ores, agglomeration of crystals and powders for the pharmaceutical use, removal of heavy metals from wastewater, soil remediation, de-inking of paper and formation of adsorbents from raw materials [2].

The particles to be agglomerated must be wetted by oil; for hydrophilic minerals it can be achieved by the use of wetting agents, e.g. surfactants. However, they usually adsorb also at the liquid-liquid interface, lowering the interfacial tension and the strength of the liquid bridges to the point that agglomerates of the desired size are destroyed by the shear forces [3, 4]. The ionic surfactant, which lowers the oil-water interfacial tension, facilitates the emulsion preparation. The presence of surfactant can also affect the attachment of an oil droplet to the particles and its spreading on the surface [5, 6].

The technical use of surfactants often involves more than one surfactant species. Mixtures of ionic surfactants have been used in a mineral flotation [7, 8]. The effect of the collector mixture in the system depends on the type and structure of collectors, and their mixing ratio. The molecules of surfactants can form not only a mixed film at the liquid-gas and liquid-solid interface but also mixed micelles. It is possible that these molecules form an insoluble complex [9].

There are many factors affecting the oil agglomeration process; the major ones are the amount and type of oil, the degree and type of agitation, pH, the density of the suspension, particle size distribution and wetting properties of the particles [10]. The strength of agglomerate depends on the interfacial tension between the two liquids, the three-phase contact angle and the ratio of the volumes of the bridging liquid and solid particles [11].

The agglomerate structure depends on the amount of oil added when relatively hydrophobic materials such as graphite or coal are used. At low volumes, loose flocs are formed; they hold together by means of pendular bridges of oil between the solid particles. With larger amounts, more compact aggregates are formed, due to the presence of funicular bridges and some water can be entrapped within the agglomerates. For a less hydrophobic mineral, e.g. pyrite, the particles tend to adsorb on the oil droplets, preventing their coalescence. Very hydrophilic particles of quartz or kaolin remain entirely within the water phase and do not attach to oil droplets. They collect around the drops and the oil flocs are formed. Such aggregates are very weak and easily broken so they are not recovered by screening [12].

## 2. Materials and methods

Tailings from the metallurgical recovery of nickel ore (the Szklary heap, Lower Silesia, Poland) were used in these investigations. The mineral material has been screened through a 40  $\mu\text{m}$  sieve. They contain a substantial amount of metallic Ni (0.08–0.22%); such a large amount is worth re-utilizing. The analysis indicated that an amorphous silicate glaze,

tridymite, calcite and graphite are the main components of the tailings. The XRD measurements were carried out using the SIMENS D5005 diffractometer, employing  $\text{CuK}\alpha$  radiation. The average particle diameter, determined using Mastersizer 2000 (Malvern), a laser diffraction instrument, was about 14  $\mu\text{m}$ . The BET surface area of the powder was 14  $\text{m}^2/\text{g}$ , as determined by Flowsorb 2300 II instrument (Micromeritics).

An anionic surfactant, sodium oleate (SOL) and a cationic surfactant, dodecyl-ammonium hydrochloride solution (DDAHCl), were used for the particles hydrophobization. The surfactant added as the second one was used as an emulsifier for kerosene. The emulsion was prepared using an ultrasonic homogenizer (Sonopuls, Bandolin). The suspension mixed with the emulsion was agitated intensively using IKA EUROSTAR 6000 overhead stirrer. The agglomerates obtained have been dried and then an average size of agglomerates ( $d_{50}$ ) has been determined using a sieve analysis.

The adsorption isotherms of modifiers have been determined by measuring the residual concentrations of surfactants in a solution after 24 h of contact with a mineral sample. All the experiments have been carried out at the pH of about 10.5, which is a natural one for tailing suspensions. The amount of the cationic surfactant in the solution has been determined by the extraction with chloroform, in the presence of dimidium bromide and disulphine blue mixed indicator. The concentration of sodium oleate has been analyzed using the extraction method described by Fowler and Steel [13].

### 3. Results

Oxide and carbonate particles are hydrophilic by nature but can be made more hydrophobic through the adsorption of a suitable surfactant. In the case of the investigated mineral tailing, which is a mixture of different components, and at the native pH of the aqueous suspension (pH = 10.5), a cationic surfactant (DDAHCl) was applied as a modifying agent. An anionic surfactant (SOL) was used as an emulsifier in agglomeration experiments.

The adsorption isotherms of surfactants on the mineral particles (Fig. 1) show that a cationic surfactant adsorbs in a greater amount than anionic one. The behaviour of isotherms can be explained by the composition of the polymineral material, containing particles which differ in charge of the surface at the native pH of the suspension. Moreover, properties of quartz can be modified by the presence of magnesium and calcium ions which can promote the adsorption of anionic surfactant molecules [14].

In the ternary system, containing a solid, aqueous solution and an organic liquid, surfactant can adsorb at various interfaces. Pre-adsorption of one type of surfactant at the mineral surface, followed by the addition of another one and kerosene, affects the oil agglomeration, changing both the shape and the size of aggregates, causing formation of paste or completely inhibiting the process [15].

It was found that the tailings cannot be successfully agglomerated with only DDAHCl or SOL added; the agglomeration was not complete and rather selective, and the shape of the aggregates was irregular. An addition of anionic surfactant reduces the amount of DDAHCl and kerosene necessary for the efficient agglomeration.

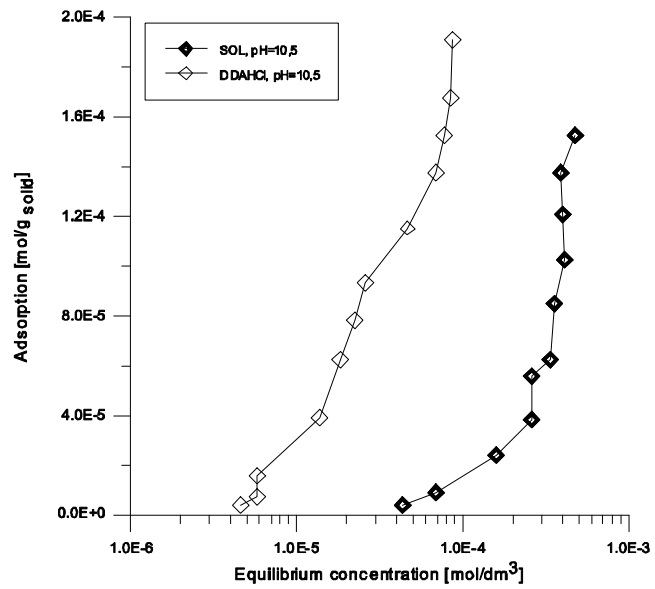


Fig. 1. Adsorption isotherms of surfactants onto the mineral particles' surface  
Rys. 1. Izotermy adsorpcji surfaktantów na powierzchni odpadów mineralnych

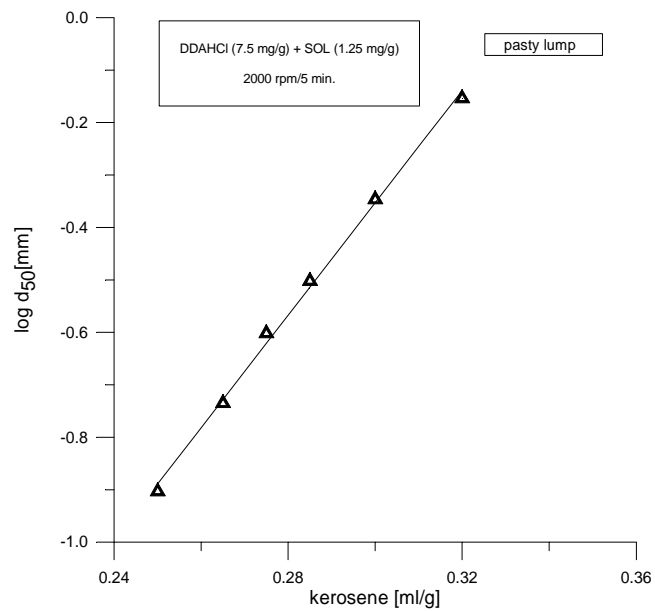


Fig. 2. Effect of kerosene amount on the common logarithm of mean diameter of agglomerates  
Rys. 2. Zależność logarytmu średnicy aglomeratów od ilości dodanej nafty

The effect of kerosene amount on the agglomerates' size can be expressed as a logarithmic correlation, as suggested by Drzymala et al. [16]. As shown in Fig. 2, the mean diameter of agglomerates increases with the increase in the quantity of kerosene. Initially, agglomerates were small, due to the insufficient amount of kerosene. As the amount of the bridging liquid was increased, the voids between particles filled with water were fading away [17]. With the larger amount of kerosene the agglomerates turned into pasty lumps and they deviated from the spherical shape.

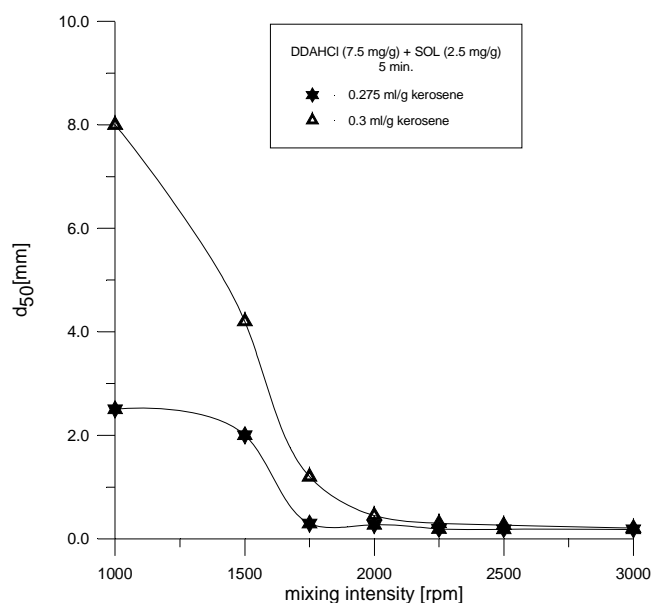


Fig. 3. Effect of the mixing intensity on the mean diameter of agglomerates

Rys. 3. Zależność średniej średnicy aglomeratów od intensywności mieszania

The mixing time and intensity of agitation play a very important role in the spherical agglomeration process. The experimental data, depicted in Fig. 3 and Tab. 1, showed that the agglomerates' diameter decreases with the agitation speed. The mean size of agglomerates changed from 8.0 to 0.15 mm when the mixing intensity increased from 1000 to 3000 rpm; the decrease was more rapid for a smaller amount of kerosene. The diameters of agglomerates were smaller at the short agglomeration time, because of insufficient oil dispersion and collisions between particles. When the agglomeration was carried out for a longer time, larger agglomerates were obtained due to an increase of an interparticle contact. When the particle-particle collision speed was increased by increasing the agitation intensity, agglomerates of a much tighter structure were formed and the largest aggregates were torn apart by shear forces [17]. Under some conditions, at less intensive mixing (1000 rpm) the paste was obtained after 15 minutes of agitation (Tab. 1).

The effect of mixing time and intensity on the size of the agglomerates  
(DDAHCl 7.5 mg/g, SOL 1.25 mg/g)

Mixing intensity [rpm]	Time							
	5 min.		10 min.		15 min.		20 min.	
	kerosene							
	0.275 ml/g	0.300 ml/g	0.275 ml/g	0.300 ml/g	0.275 ml/g	0.300 ml/g	0.275 ml/g	0.300 ml/g
	$d_{50}$							
1000	2.50	8.00	3.80	9.50	5.50	paste	10.50	paste
1500	2.00	7.30	0.27	8.00	0.35	10.00	0.27	3.85
1750	0.30	1.20	0.30	5.54	0.34	4.80	0.28	7.00
2000	0.25	0.45	0.22	0.35	0.30	0.35	0.21	0.27

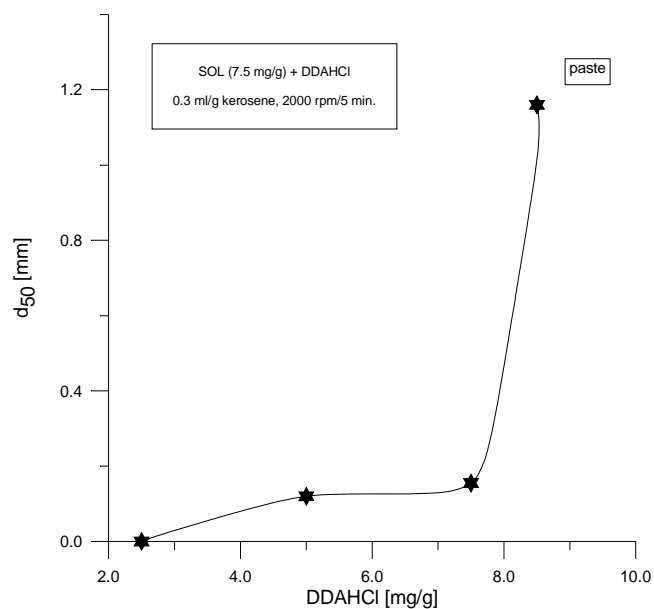


Fig. 4. Effect of the amount of DDAHCl on the mean diameter of agglomerates

Rys. 4. Zależność średniej średnicy aglomeratów od ilości dodanego chlorowodoru dodecyloaminy

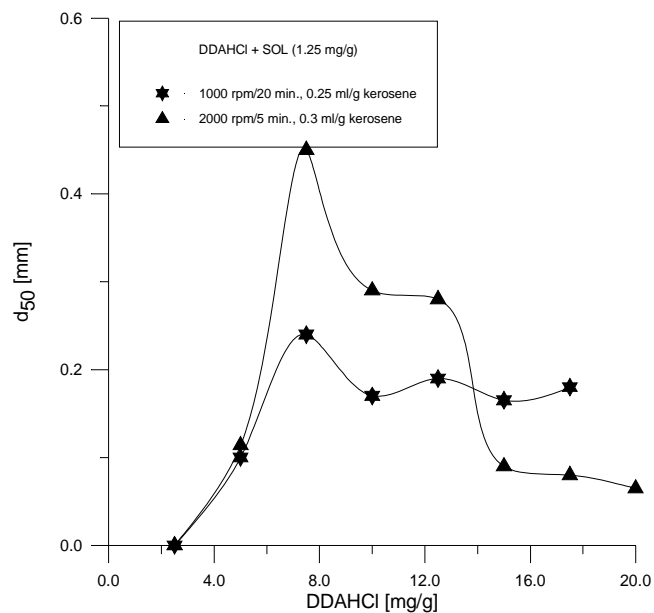


Fig. 5. Effect of the amount of DDAHCl on the mean diameter of agglomerates

Rys. 5. Zależność średniej średnicy aglomeratów od ilości dodanego DDAHCl

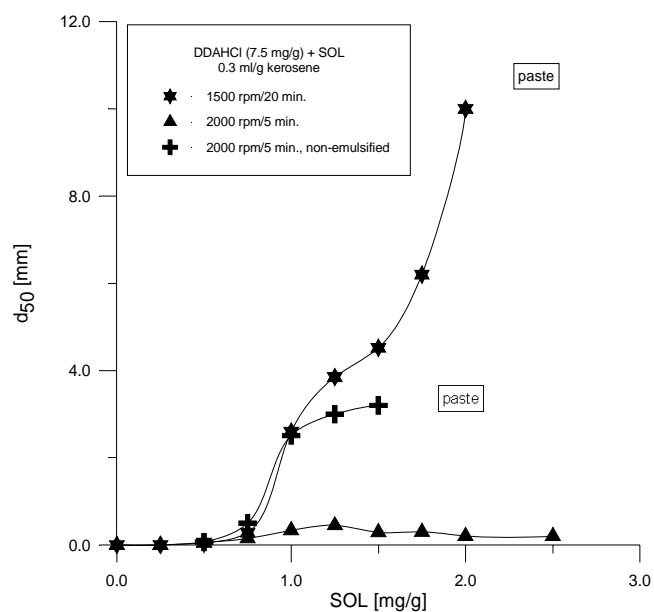


Fig. 6. Effect of the amount of sodium oleate on the mean diameter of agglomerates

Rys. 6. Zależność średniej średnicy aglomeratów od ilości dodanego oleinianu sodu

The effect of the nature of surfactant and its amount on the agglomeration outcomes are presented in Figs 4–6. The order of surfactant added has a very significant effect on the agglomeration results. When sodium oleate is used as the first modifier (Fig. 4), an increase in the amount of dodecylammonium hydrochloride used to prepare the kerosene emulsion causes an increase in agglomerates' diameter, and finally the paste is formed. With the reverse order of addition (Fig. 5), the size of agglomerates increases with the amount of cationic surfactant, until the concentration of DDAHCl is about 7.5 mg/g, then the diameter drops dramatically. Too high concentration of surfactant in a solution lowers the surface tension and the strength of oil bridges between particles; these effects are unfavourable for the oil agglomeration [3, 18]. Emulsification of oil in the presence of surfactant lowers the amount of bridging liquid essential to the agglomeration of particles, due to a reduction in oil droplets' size [6]. As shown in Fig. 6, a larger amount of sodium oleate in kerosene emulsion causes the growth of aggregates and the paste formation. However, ultrasound emulsification of kerosene in anionic surfactant solution brings about a better dispersion of oil droplets, and the agglomerates of a tighter structure are obtained. The description of the system is complex, due to the presence of three separate phases (solid-water-oil). The co-existence of cationic and anionic surfactant's molecules which adsorb at the particle/solution and oil/solution interfaces makes the system even more complicated. This situation is similar to the flotation process, where mixed collector systems are used in some cases [7].

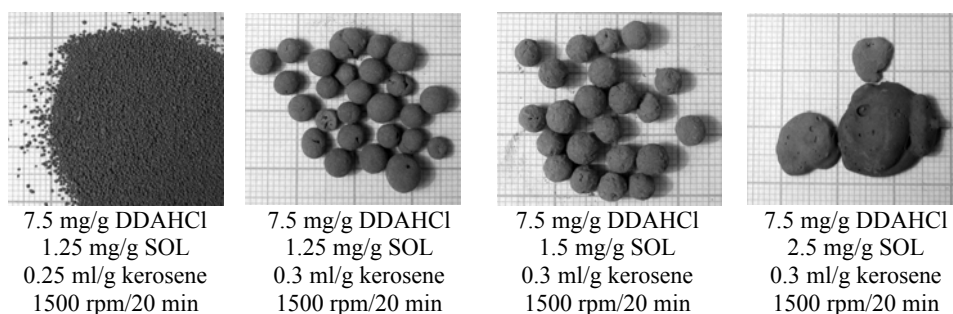


Fig. 7. Pictures of some exemplary agglomerates of the mineral tailings from the Szklary heap

Rys. 7. Zdjęcia przykładowych aglomeratów z odpadów mineralnych z hałdy Szklary

Some exemplary agglomerates of mineral tailings were presented in Figure 7. One can see very small particles, well developed agglomerates and pasty lump.

#### 4. Conclusions

The adsorption isotherms of surfactants indicate that both of them adsorb at the mineral surface under equilibrium conditions, and the amount of adsorbed cationic surfactant is higher due to the high content of silicates in the sample.

The mineral tailings from the Szklary heap can be agglomerated using dodecylammonium hydrochloride and sodium oleate.



The agglomeration process can be realized with kerosene as a bridging liquid.

The addition of lone cationic surfactant is not sufficient to agglomerate particles.

The effect of bridging the oil amount on the agglomerates' size can be expressed as a logarithmic correlation. The mean diameter of agglomerates increases with the increase of the quantity of kerosene.

The agglomerates' diameter decreases with the agitation speed. When the agglomeration was carried out for a longer time, larger agglomerates were obtained due to an increase in an interparticle contact.

The order of surfactant addition has a very significant effect on the agglomeration results. When sodium oleate is used as the first modifier, the amount of dodecylammonium hydrochloride for preparing the kerosene emulsion increases, which causes the increase in the agglomerates's diameter, and finally the paste is obtained.

With the reverse order of surfactant addition, the size of agglomerates increases with the amount of cationic surfactant, until the concentration of DDAHCl is about 7.5 mg/g. Then the diameter of agglomerates decreases dramatically.

Increase of the sodium oleate amount in kerosene emulsion causes the growth of aggregates and the paste formation.

The ultrasound emulsification of kerosene in anionic surfactant solution brings about a better dispersion of oil droplets, and the agglomerates of a tighter structure are obtained.

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