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FLOTATION AFTER A DIRECT CONTACT OF FLOTATION REAGENTS WITH CARBONATE PARTICLES PART 1. MODEL INVESTIGATIONS

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Abstract: Carbonate fluorapatite (francolite), calcite and dolomite separately, as well as their model mixtures, were subjected to flotation after conditioning the particles with microemulsion consisting of 20% of Custafloat AR27 (collector, blend of fatty acid soaps and sulfates), 55% fuel oil #5 and 25% water at 70% solids density and subsequent pulp dilution with water to 25% solids. The best separation of carbonate fluorapatite from calcite and dolomite occurred at pH 8.5 and microemulsion dose between 0.9 and 1.5 kg/Mg, 1.5 min conditioning time and 2 minutes of flotation time. The obtained flotation concentrates using 1.5 kg/Mg of collector contained 84% carbonate fluorapatite (34% P₂O₅) with 84% recovery. The 84/84 separation efficiency in terms of grade-recovery indices points to promising results which can be obtained for real phosphate ores.

Keywords: phosphates, flotation, microemulsion, separation

Introduction

Ores and other raw materials can be processed by different methods including gravity, hydraulic, magnetic, electric and other separations as well as by coagulation, oil agglomeration and flotation (Wills and Napier-Munn, 2006). Among beneficiation methods, flotation is used the most often because of its superior efficiency in many application (Drzymala, 2007). There are different modifications of flotation because it responds well to variation of operational variables and applied reagents. As a result, there is a constant search for flotation improvements. One of recent modifications is a direct contact of particles with flotation reagents in the form of microemulsions or similar structures (Ahmed, 2005; Ahmed and Drzymala, 2004, 2012) and subsequent

flotation after dilution of the pulp with water. This method differs from the traditional approach in which the particles are brought into contact with aqueous solutions or emulsions of the flotation reagents. The direct contact approach tends to overcome the problem of insufficient adsorption of flotation reagents, especially in the case when oil is used as the flotation collector or extender and the surface of particles is not able to absorb it. It happens for instance in the flotation of oxidized coal because the adsorption of oil on hydrophilic coal surfaces is significantly reduced. To increase the chance of oil and other flotation reagents to be adsorbed, it was proposed to change the procedure of flotation. In this approach, particles are contacted with reagents either in the absence of water or with reagents forming with water special structures such as microemulsion or liquid crystals. Next, the pulp is diluted with water to slurry density typical in froth flotation. It was proved that this modification works very well for highly oxidized coals (Ahmed and Drzymala, 2012) because there was no flotation when the flotation reagents were added to the aqueous suspension and very good coal flotation in the case of the direct contact approach. In this paper the separation efficiency using the direct contact technique and flotation will be investigated for a model carbonate fluorapatite-calcite-dolomite system while in another paper, part 2 of this paper, the case of phosphate ores will be presented. Phosphates were selected for investigations because they are a global resource of phosphorus, an essential element for plant and animal nutrition (Negm and Abouzeid, 2008). However, there is a constant depletion of the high-grade phosphates (Negm and Abouzeid, 2008), so there is a need to optimize the available mineral processing technologies, to maximize the benefits of the low-grade phosphate resources in a more efficient manner, and to minimize the associated wastes. This can be achieved by looking for new processing technologies or adaptation of recent innovations in the classical upgrading techniques including flotation. However, flotation has its limitation in treating low grade phosphate ores in addition to the high price of some reagents used. Therefore, this paper aims at modifying the classical flotation technique to improve flotation of low grade phosphate ore. We will test the approach of direct contact of flotation reagents with particles before flotation for separation of carbonate fluorapatite from the calcite and dolomite gangue.

Experimental

Minerals

Carbonate fluorapatite (francolite, $\text{Ca}_5(\text{PO}_4)_{2.5}(\text{CO}_3)_{0.5}\text{F}$), dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) and calcite (CaCO_3) were investigated. Carbonate fluorapatite was obtained from Ma'aden Company while dolomite and calcite from Saudi Carbonate Co. Ltd. Their identity and purity was checked by the X-ray analysis. The minerals were dry crushed in a jaw crusher and wet ground in a ball mill to get the size fraction below 0.25 mm.

Reagents

For the direct contact (conditioning) stage we used microemulsion ME1 (Fig. 1) consisting of collector (Custafloat AR27, a blend of fatty acid soaps and sulfates), oil (extender, fuel oil #5) and water. The phase diagram of the Custafloat AR27 - fuel oil #5 - water system is presented in Fig. 1. It was constructed using a water titration method at ambient temperature. The mixtures of oil and collector, at certain weight ratios, were mixed with water added as drops, under moderate stirring with a magnetic bar. After being equilibrated at ambient temperature for 24 hours, the system was visually analyzed under strong light to detect microemulsions, emulsions and other structures. The findings were confirmed by measuring transmittance using a Digital D-801 Photocon colorimeter at the 570–590 nm wavelength (Chen et al., 2004).

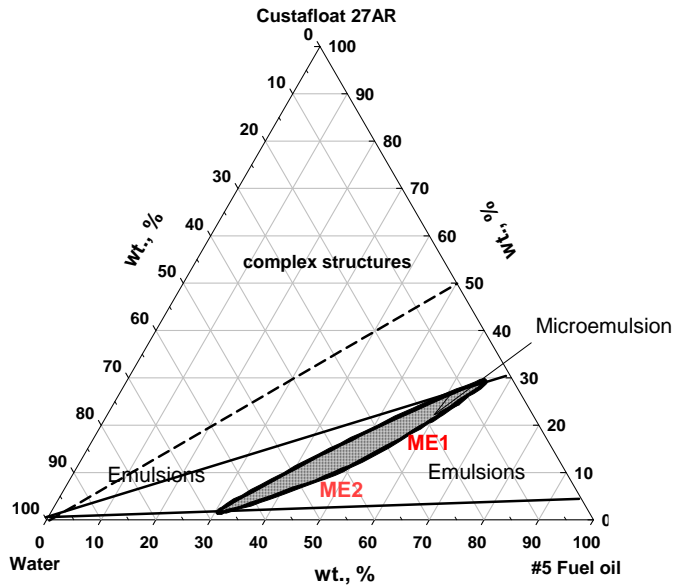


Fig. 1. Ternary collector-oil-water phase diagram showing used in experiments microemulsion ME1 region and composition

The phase diagram shows that the investigated collector-fuel oil-water system is able to form microemulsions. The shape of the microemulsion area is like a lens. The lower boundary of the lens is represented by a line having collector-to-fuel oil ratio of approximately 1:19, while the upper boundary is determined by the collector-to-fuel oil ratio of 1:2.33. The lens is oriented from the bottom towards the higher water content and from the top towards the lower water content. This indicates that the microemulsion, called ME2, starts to form at low collector concentrations and high water content. This can be attributed to the fact that in the presence of water, the

collector starts to act as a surfactant which accumulates at the water-oil interface leading to more stable droplets. On the other hand, microemulsion ME1 is formed at low water concentrations (top head of the lens), but at a higher collector amount. In our investigation we will use ME1 because of smaller amount of water in its structure. Preliminary tests with carbonate fluorapatite showed superiority of ME1 over ME2. The weight fractions of ME1 were 20% collector, 55% oil and 25% water with a collector-to-oil ratio of 20:55, which is equivalent to 1:2.75.

The phase diagram also shows that at the collector concentration less than 30% an emulsion is formed, while higher concentrations of the collector lead to the formation of a complex reagents structure. Usually these complex structures hamper flotation as it was observed by Ahmed (2005) during oxidized coal flotation.

Flotation tests

Flotation tests were carried out in a D-12" Denver flotation cell equipped with a 1 dm³ flotation tank. Tap water was used in all the tests. After establishing the collector-oil-water phase diagram (Fig. 1), the flotation tests were performed using a special procedure. In this procedure the flotation reagents in the form of microemulsion were added to a single, binary or tertiary pure mineral(s)-water system and conditioned at a high solid percent equal to 70%. The reagentized pulp was diluted to the targeted solid/liquid ratio and aerated for initiation of flotation. The different obtained products were collected, dried and weighted. In the case of binary and ternary pure minerals mixtures, they were subjected either to mineralogical or chemical analyses for determination of flotation performance. In single pure mineral flotation in the presence of microemulsions, different parameters such as conditioning time, conditioning pH, flotation pulp solids content and microemulsion dosage were investigated. The determined optimum conditions were applied for binary or ternary pure mineral systems as simulation of real ore flotation. It is worth mentioning that the aeration rate and flotation time were kept constant for the entire test program. The impeller speed was 1200 rpm in all the tests.

Results and discussion

Pure minerals flotation using a direct contact with microemulsion ME1

The first parameter that has been taken into consideration when using ME1 for flotation of pure minerals is the microemulsion conditioning time with pure single minerals. This was so because the conditioning time is an important parameter in determining the amount of microemulsion to be adsorbed on the mineral surface. The results of this series of experiments along with some additional process parameters (conditioning pulp density 70%, natural pH, microemulsion dosage of 0.5 kg/Mg) are given in Fig. 2. It shows that at the applied microemulsion dose, the carbonaceous gangue yield is small and is not highly affected by the conditioning time. On the other

hand, the carbonate fluorapatite recovery to the concentrate is affected by the conditioning time and varies from 70 to approximately 98% with maximum at 1.5 min of conditioning. The reduced recovery at a short conditioning time may be attributed to incomplete adsorption of microemulsion on the carbonate fluorapatite surface. With increasing conditioning time, the adsorption increases, leading to an increase in the carbonate fluorapatite recovery. Longer conditioning times result in decreasing carbonate fluorapatite recovery. This effect can be attributed to mechanical removal of microemulsion from the carbonate fluorapatite surface and decomposition of the microemulsion by cations coming from the carbonate fluorapatite surface into the solution. The obtained result indicates that the 1.5 min conditioning time is sufficient and it will be used in the subsequent experiments.

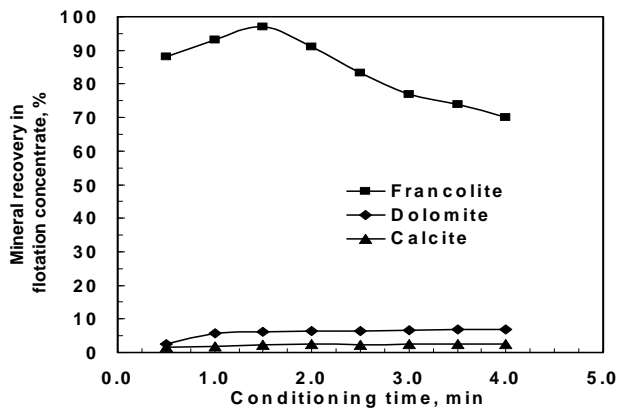


Fig. 2. Effect of conditioning time on single mineral flotation recovery using 0.5 kg/Mg of ME1 (pH = 8.5, solids density: conditioning 70%, flotation 25%)

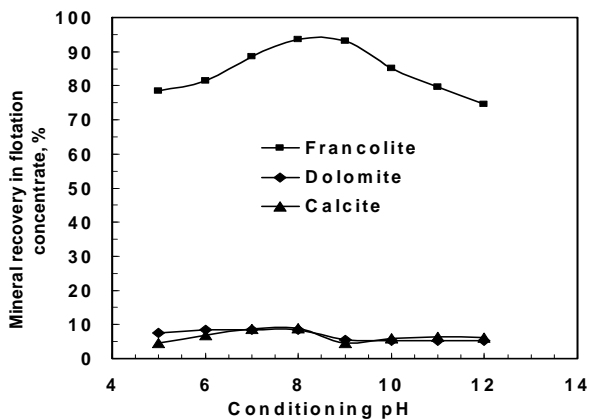


Fig. 3. Effect of conditioning pH on single mineral flotation recovery using 0.5 kg/Mg of ME1 (conditioning: time 1.5 min, solids density 70%; flotation: time 2 min, pH 8.5, solids density 25%)

Another important parameter which controls reagents adsorption on the solid surface is conditioning pH. The conditioning pH was changed from 5 to 12 and the obtained results are plotted in Fig. 3. According to Fig. 3 the optimum conditioning pH is 8.5. In fact, this supports the interpretation of the pH effect in the case of conditioning time optimization previously assumed.

The next studied parameter was solid content in the pulp (Fig. 4). It can be seen that the solid content providing the best recovery of carbonate fluorapatite is about 25%.

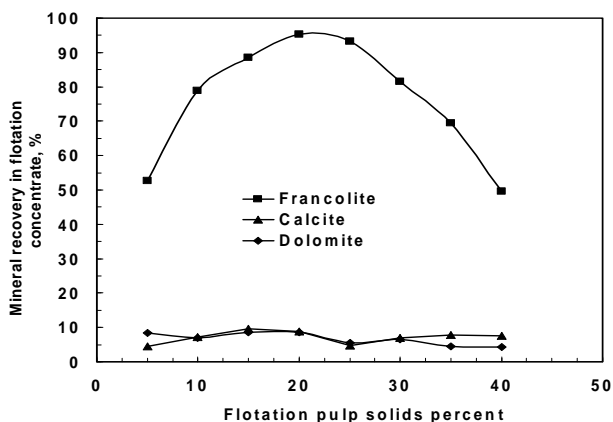


Fig. 4. Effect of flotation pulp solids content on single mineral flotation recovery using 0.5 kg/Mg of the ME1 (conditioning: time 1.5 min, solids density 70%, pH = 8.5; flotation time: 2 min, pH 8.5, solids density variable)

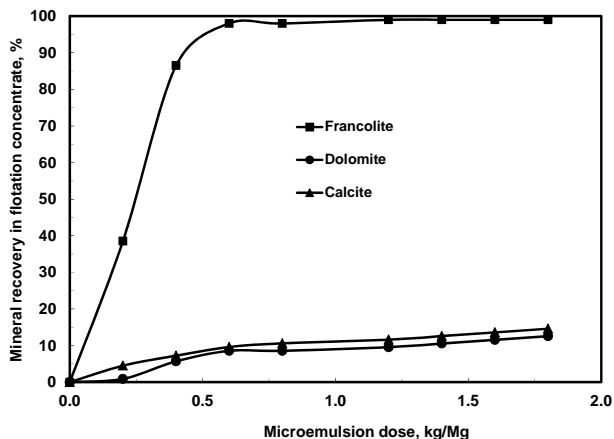


Fig. 5. Effect of microemulsion dose on single mineral flotation recovery using ME1 (conditioning: time 1.5 min, solids density 70%, pH = 8.5, emulsion dose variable; flotation: time 2 min, pH 8.5, solids density 25%)

The hitherto determined favorable conditions were used to determine the dose of the microemulsions. The dose was changed from 0.1 to approximately 1.8 kg/Mg. The obtained results are shown in Fig. 5. The figure shows that the carbonate fluorapatite recovery increases sharply up to about 0.6 kg/Mg when the recovery is almost complete.

Two pure minerals mixtures flotation using microemulsion ME1

In this set of experiments, two separate mixtures were formed. The first mixture was composed of pure carbonate fluorapatite mixed with pure dolomite while the second mixture was made of pure carbonate fluorapatite mixed with pure calcite. The carbonate fluorapatite-to-dolomite ratio of the first mixture was 1:1 by weight while the carbonate fluorapatite-to-calcite ratio in the second mixture was 2:1 by weight. These ratios of mixing were selected to simulate the mineralogical ratios observed in many phosphate ores (Al-Wakeel, 2005).

The effect of microemulsion dose on flotation of carbonate fluorapatite either from the carbonate fluorapatite-dolomite mixture or carbonate fluorapatite-calcite mixture was investigated. In both sets of experiments, the operating conditions were kept constant as previously determined for single pure minerals flotation (conditioning: time 1.5 min, pH = 8.5, solids density 70%; flotation: time 2 min, pH 8.5, solids density 25%) for carbonate fluorapatite-to-dolomite ratio as 1:1. Figure 6 shows the flotation response with microemulsion ME1 for the carbonate fluorapatite-dolomite mixture while Fig.7 for the carbonate fluorapatite-calcite mixture.

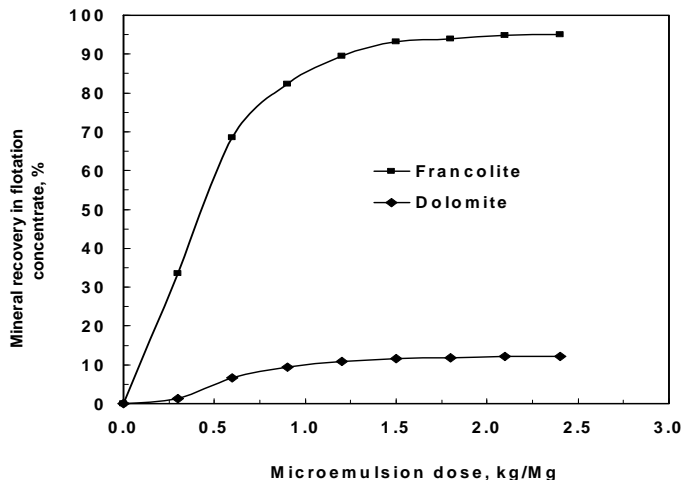


Fig. 6. Effect of microemulsion (ME1) dose on carbonate fluorapatite flotation from carbonate fluorapatite-dolomite binary mixture (conditioning: time 1.5 min, pH = 8.5, solids density 70%; flotation: time 2 min, pH 8.5, solids density 25%) (carbonate fluorapatite: dolomite ratio 1:1)

It can be seen in Figs 6 and 7 that the recovery of minerals in both systems increases with the dose of microemulsion and the recovery of francolite reaches 95% while for dolomite and calcite the recovery is about 15%. Thus, the separation of carbonate fluorapatite by flotation from binary mixtures with either dolomite or calcite is very efficient.

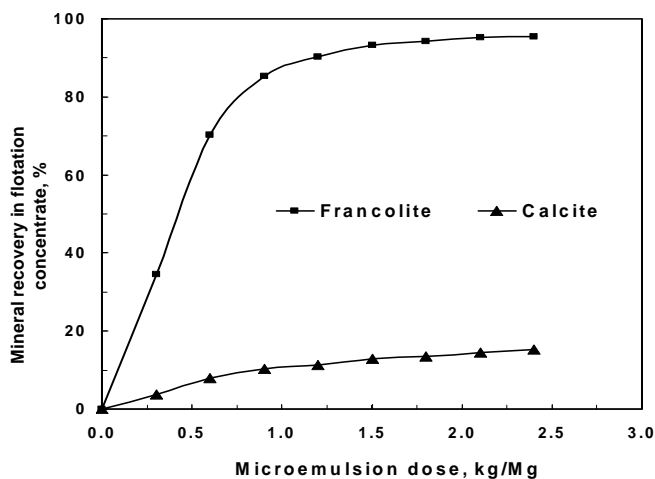


Fig. 7. Effect of microemulsion ME1 dose on carbonate fluorapatite flotation from carbonate fluorapatite-calcite binary mixture (conditioning: time 1.5 min, pH = 8.5, solids density 70%; flotation: time 2 min, pH 8.5, solids density 25%) at carbonate fluorapatite-to-calcite ratio equal to 2:1

It can be noticed that the plateau at 95% recovery of carbonate fluorapatite from the binary mixture using microemulsions is lower than that in the case of single pure mineral flotation using the same microemulsion ME1 because the recovery is 99% (Fig. 5). This may be attributed to some microemulsion consumption by dolomite and calcite.

Three pure minerals mixture flotation using microemulsion ME1

In a trial to simulate a real phosphate ore, a synthetic mixture of carbonate fluorapatite, dolomite and calcite were made. The minerals ratios in the artificial mixture were as 2:2:1 by weight of carbonate fluorapatite, dolomite and calcite, respectively. Flotation of carbonate fluorapatite from this mixture was tried using different doses of microemulsion ME1. The operating conditions were as follows: conditioning: time 1.5 min, pH = 8.5, solids density 70%; flotation: time 2 min, pH 8.5, and solids density 25%. The obtained results are presented in Fig. 8.

According to Fig. 8 a good separation of carbonate fluorapatite from the ternary mixtures by flotation occurs at the microemulsion dose from 0.9 to 1.5 kg/Mg. At 1.5 kg/Mg the concentrate contains 83.6% carbonate fluorapatite. Microemulsion dosages lower than 0.9 kg/Mg provided less favorable results.

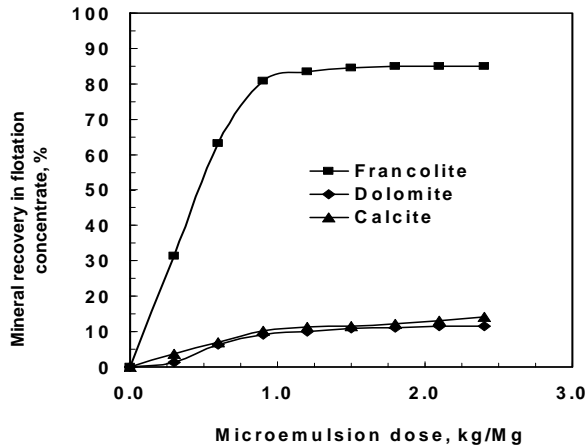


Fig. 8. Effect of microemulsion ME1 dose on carbonate fluorapatite flotation from carbonate fluorapatite-dolomite-calcite (2:2:1) ternary mixture (conditioning: time 1.5 min, pH=8.5, solids density 70%; flotation: time 2 min, pH 8.5, solids density 25%)

The results from Fig. 8 were replotted as the grade-recovery Halbich upgrading curve to see better the possible separation results for phosphate ores containing carbonate fluorapatite using the approach of the direct contact of flotation reagents forming microemulsion and interacting with particles at high solids densities, and subsequent flotation after dilution of the slurry to typical densities. Figure 9 shows that this approach provides high quality concentrates (above 33% of P_2O_5) with reasonable P_2O_5 recovery of about 85%. The calculations are based on the assumption that the investigated carbonate fluorapatite (francolite) contains 40% of P_2O_5 (Melike et al., 2011).

The results obtained in this study indicate a possibility of using microemulsion for upgrading phosphates. The noticeably shortcoming of special concern is a relatively high dose of microemulsion needed. A dose of 0.6 kg/Mg of microemulsion was enough to recover more than 90% of carbonate fluorapatite when it was floated alone. This dose has increased to approximately 0.8 kg/Mg to recover about 85% of carbonate fluorapatite when floated from binary mixtures containing dolomite or calcite and now the dose has increased to above 0.9 kg/Mg. The high dose required in this case may be attributed to the fact that the mixture was not deslimed. This may lead to a high surface area requiring a high dose of microemulsions for surface coverage and flotation. One more reason is that the high surface area of the carbonaceous minerals may lead to a noticeable increase in Ca^{2+} ions concentration in the solution and thus disturb the microemulsion droplets.

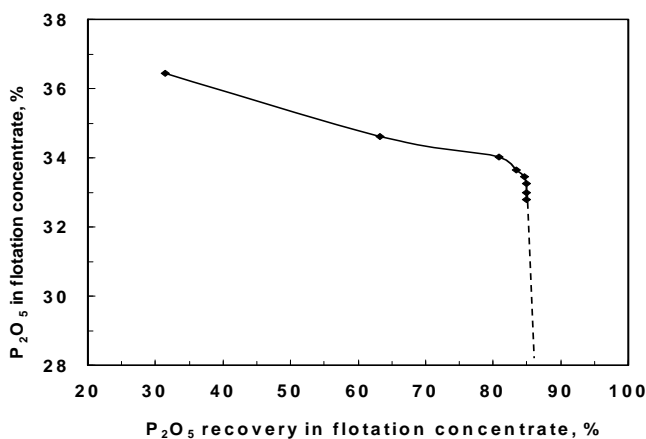


Fig. 9. Carbonate fluorapatite (francolite) separation from tertiary carbonate fluorapatite–dolomite–calcite model mixtures by flotation after a direct contact of flotation reagents forming microemulsion and reacting with particles at 70% solids density and subsequent dilution to 25% solids density in terms of the Halbich grade (P_2O_5)-recovery (P_2O_5) upgrading curve

Conclusions

It results from the flotation tests conducted at pH 8.5 on a model carbonate fluorapatite–dolomite–calcite system that a direct contact of the flotation reagents forming microemulsion and consisting of 20% of collector, 55% oil, and 25% water with particles at solids density 70% and subsequent dilution of the system with water to form flotation aqueous suspension of 25% density, provide high quality carbonate fluorapatite concentrates containing for instance 83.6% carbonate fluorapatite with 84.6% carbonate fluorapatite recovery when the microemulsion dose of the microemulsion is 1.5 kg/Mg. Negligible separations were achieved when the microemulsion–particles direct contact stage was eliminated. The 84/84 separation efficiency, in terms of the francolite content in concentrate - francolite recovery, points to promising results which can be expected during beneficiation of real phosphate ores. Therefore, the obtained results will be verified with a low quality phosphate ore.

References

- ABOUZEID M. Abdel-Zaher, 2008. *Physical and thermal treatment of phosphate ores – An overview International Journal of Mineral Processing*, Vol. 85, Issue 4, 59–84.
- AHMED A.M.H., 2005. *Application of microemulsion for upgrading difficult-to-float materials*. Ph.D. thesis, Faculty of Mining Geengineering and Geology, Wroclaw University of Technology, Poland.
- AHMED A.M.H., DRZYMALA J., 2012. *Upgrading difficult-to-float coal using microemulsion*, Minerals & Metallurgical Processing, Vol. 29, No. 2: 75–83.

- AHMED A.M.H., DRZYMALA J., 2004. *Effect of flotation procedure and composition of reagents on yield of a difficult-to-float coal*, Physicochemical Problems of Mineral Processing, 38, 53–63.
- AL-WAKEEL M. I., 2005. *Effect of mechanical treatment on the mineralogical constituents of Abu-Tartour phosphate ore, Egypt*, International Journal of Mineral Processing, Vol. 75, Issues 1–2, 101–112.
- CHEN H., CHANG X., WENG T., ZHAO X., GAO Z., YANG Y., XU H., YANG, X., 2004. *A study of microemulsion systems for transdermal delivery of triptolide*. J. Control. Rel. 98: 427–436.
- DRZYMALA J., 2007. *Mineral Processing. Foundations of theory and practice of mineralurgy*, Oficyna Wyd. PWr., Wrocław, 507 pages, <http://www.dbc.wroc.pl/Content/2070/Drzymala.pdf>
- MELIKE SINIRKAYA, A. KADIR ÖZER, M. SAHIN GÜLABOĞLU, 2011. *Investigation of the changes of P₂O₅ content of phosphate rock during simultaneous calcination/sulfation*, Powder Technology, Vol. 211, Issue 1, 72–76.
- NEGM A.A., ABOUZEID A.Z.M., 2008. *Utilization of solid wastes from phosphate processing plants*, Physicochemical Problems of Mineral Processing, 42, 5–16
- WILLS B.A., NAPIER-MUNN T.J., 2006. *Wills; Mineral Processing Technology*, Elsevier, Amsterdam.

