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Gamma processes of shear flocculation, oil agglomeration and liquid–liquid extraction

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A R T I C L E I N F O

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A B S T R A C T

Gamma flotation process is characterized by emphasis on the control of solution surface tension and the separation of minerals in suspension with this technique is based on the differences in wettability of minerals. The wettability properties of mineral surfaces can be defined in terms of their values of critical surface tension of wetting (γ_c) as a quantifying parameter, which is an essential property to achieve selectivity in surface chemistry-based separation processes. That is, the gamma flotation technique utilizes the differences in the critical surface tension of wetting (γ_c) of minerals. Similar to the flotation method, shear flocculation, oil agglomeration and liquid–liquid extraction processes also utilize differences in wettability of minerals. Therefore, the separations of minerals by the control of surface tension in the shear flocculation, oil agglomeration and liquid–liquid extraction methods can be provided. In this study, the separations of some minerals with these processes have been investigated by using the control of the solution surface tension and the successful results could be reached. Consequently, these new separation processes have been defined as 'gamma shear flocculation', 'gamma oil agglomeration' and 'gamma liquid–liquid extraction'.

1. Introduction

As the grade of mineral deposits decreases, the valuable minerals often appear in the form of finely disseminated grains in an ore. Therefore, size reduction by crushing and grinding is required to liberate the valuable constituents. However, fine particles produced during the comminution processes decrease the efficiency of the concentration processes in mineral processing operations. Therefore, there is considerable interest in developing a process that could successfully handle such fine particles [1,2]. Shear flocculation is the aggregation of fine particles in a convenient stirring regime after hydrophobization by the adsorption of surfactants [3]. Oil agglomeration and liquid–liquid extraction are important separation techniques among oil-assisted fine particle processing processes [4]. In the oil agglomeration technique, hydrophobic minerals in aqueous suspensions are aggregated by oil droplets since oil preferentially wets the hydrophobic surfaces. Solid particles, therefore, can be bridged by the second liquid which is immiscible with the medium in which the process takes place [4,5]. In the case of liquid–liquid extraction process, large amounts of organic and aqueous phases are contacted and the minerals, depending on their hydrophobicity, transfer either to the aqueous or organic phases. Both processes are only possible when the treated minerals are sufficiently hydrophobic so that they are selectively wetted in water by oil [4,6].

The wettability properties of mineral surfaces can be defined in terms of their values of 'critical surface tension of wetting (γ_c)', which is an essential characteristic in achieving selectivity in surface chemistry processes such as flotation, shear flocculation, oil agglomeration and liquid–liquid extraction [7,8]. The contact angle (θ) has been extensively used to assess the hydrophobicity or wettability degree of the minerals or solids in mineral processing theory and practice. Shafrin and Zisman [9] found that the contact angle (θ) of a sessile liquid drop on a solid surface decreases in tandem with decrease of the air–liquid interfacial tension. Thereafter, Yarar and Kaoma [10] reported that the flotation recovery of minerals decreases as decrease of the air–liquid interfacial tension of the liquids used as flotation medium. Similar to the flotation behavior of minerals, the shear flocculation, oil agglomeration and liquid–liquid extraction recoveries of minerals also decrease with decreasing the air–liquid interfacial tension. Eventually, while the flotation and shear flocculation of minerals do not occur at the air–liquid interfacial tensions below 'the critical surface tension of wetting (γ_c)' value of the mineral [10,11], the oil

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agglomeration and liquid–liquid extraction processes of minerals do not take place at the air–liquid interfacial tensions lower than 'the critical solution surface tension ($\gamma_{\text{c-a}}$) for oil agglomeration' and 'the critical solution surface tension ($\gamma_{\text{c-e}}$) for liquid–liquid extraction', respectively. Also, it has been reported that the $\gamma_{\text{c-a}}$ and the $\gamma_{\text{c-e}}$ parameters are essentially the same, which are slightly higher than the γ_{c} value of the mineral [12–14].

The gamma flotation process, which operates on the basis of solution surface tension control to facilitate the separation of inherently hydrophobic solids, is based on the differences in wettability of minerals [15]. The use of the critical surface tension of wetting (γ_{c}) differences of two hydrophobic solids by controlling the surface tension of the solution in which they are suspended plays a key role in this process. One of the solids, which its γ_{c} value is greater than solution surface tension (γ_{LV}), is wetted by the solution and the other solid whose γ_{c} value is lower than γ_{LV} can attach air bubble and float. Therefore the separation of two solids in suspension can be generated [15].

In this study, similar to the gamma flotation process, the separations of some minerals with shear flocculation, oil agglomeration and liquid–liquid extraction techniques by using the control of the solution surface tension have been investigated depending on the critical values of the solution surface tension. This critical value is 'the critical surface tension of wetting (γ_{c})' in the shear flocculation method. In the oil agglomeration and liquid–liquid extraction techniques, 'the critical solution surface tension ($\gamma_{\text{c-a}}$) for oil agglomeration' and 'the critical solution surface tension ($\gamma_{\text{c-e}}$) for liquid–liquid extraction' are the critical parameters, respectively. Consequently, this paper aims to introduce the gamma processes of shear flocculation, oil agglomeration and liquid–liquid extraction as new separation methods for fine particle processing.

2. Experimental

2.1. Materials

The experiments were carried out using high purity samples of celestite ($SrSO_4$) from Barit Maden Turk A.S., magnesite ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$) from Kalemaden Company, Turkey. The chemical analysis results of these samples are given in Table 1. The samples were dry ground for below 38 μm size fraction in a ceramic ball mill. The particle size analysis of the ground samples were determined by an Andreasen pipette and the 80% passing sizes of the particle size distributions of the celestite, magnesite and dolomite samples were found to be 30, 24 and 25 μm, respectively. Sodium oleate ($C_{17}H_{33}COONa$) as anionic surfactant was used to render the hydrophobization of mineral surfaces. Sodium oleate was prepared from oleic acid with a chemical formula of $C_{17}H_{33}COOH$ manufactured by Carlo Erba Company and sodium hydroxide produced by Merck Company. In the oil agglomeration and the liquid–liquid extraction experiments, kerosene was used as bridging liquid and organic phase, respectively. The chemicals used in the experiments were of analytical grade and distilled water was employed for all experimental work.

Table 1
The chemical compositions of the mineral samples used in the experiments.

Chemical composition, %	Celestite	Magnesite	Dolomite
SrO	55.87		
MgO		46.09	19.04
CaO	0.24	1.12	29.38
Al_2O_3			1.39
Fe_2O_3		0.24	0.14
SiO_2		1.76	4.40

2.2. Solution surface tension measurements and chemical analysis

Methanol (>99.9% in purity), purchased from Merck, was used to obtain the desired surface tension of solutions. The solution surface tension (γ_{LV}) values of methanol–water solutions were measured by the pendant-drop method [16] using the KSV CAM 101 goniometer. The measurements were performed using a hook syringe. Four measurements were made for each data point and the average values were reported. The measured values of the surface tensions of the methanol–water solutions are close to the data in the literature [17].

The products obtained from the gamma processes of shear flocculation, oil agglomeration and liquid–liquid extraction were analyzed by GBC Atomic Absorption Spectrophotometer (AAS) for their Sr content. The grades of celestite and/or dolomite of the products were also calculated.

2.3. Experimental

The shear flocculation, oil agglomeration and liquid–liquid extraction experiments were carried out in a 400 cm^3 cylindrical cell. Four baffles were attached to the interior surface of the cell in order to obtain a homogeneous suspension and to provide the maximum collision efficiency of the suspended particles. The stirring of the suspension was made by a centrally located turbine impeller with four blades. All experiments were performed at the natural pH values of the mineral suspensions.

2.3.1. Gamma shear flocculation experiments

The flocculation experiments were made using 1 g mixtures (1:1) of celestite + magnesite and dolomite + celestite and 300 cm^3 methanol–water solutions. The mixture was pre-conditioned for 1 min in order to obtain a well-dispersed suspension. Thereafter, the dispersed suspension was conditioned with sodium oleate at an impeller speed of 500 rpm for 3 min. At the end of the surfactant conditioning time, a settling time of 1 min for the suspension was allowed. Thereafter, the supernatant containing non-flocculated material was taken out, at a fixed distance of 4.5 cm below the air–liquid interface, by siphon system using a convenient pipe. The settled material was filtered, dried and weighed.

2.3.2. Gamma oil agglomeration experiments

The celestite + magnesite and dolomite + celestite mixtures prepared using 2.5 g of each mineral sample were pre-conditioned for 1 min to achieve well-dispersed suspensions of 300 cm^3. Thereafter, the dispersed suspension was conditioned for 2 min with sodium oleate at impeller speeds of 1250 and 1500 rpm for celestite + magnesite and dolomite + celestite mixtures, respectively. The stirring speeds studied in the gamma oil agglomeration and the gamma shear flocculation experiments were the optimized values for these minerals in our previous studies [18,19]. After the surfactant conditioning time, 1 cm^3 of kerosene was added into the suspension and conditioned to form agglomerates for another 3 min of agglomeration time. Then, the obtained agglomerates were separated from suspension using a 53 μm test sieve. The agglomerates remained on the test sieve were washed in the same manner using a pisette with approximately 500 cm^3 of solution that has the same surface tension used in the experiment. The obtained agglomerates were dried in an oven and then weighed.

2.3.3. Gamma liquid–liquid extraction experiments

In the liquid–liquid extraction experiments, 80 cm^3 of methanol–water solution as aqueous phase and 20 cm^3 of kerosene as organic phase were used. The mixtures of celestite + magnesite and dolomite + celestite were obtained using 0.125 g from each mineral. To provide a well-dispersed suspension, the mixture