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Separation of huntite and hydromagnesite from magnesite in combination of physicochemical treatment and size reduction

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ABSTRACT

Huntite and hydromagnesite are important minerals in the synthesizing of fire-safe composites. They are mostly not pure and associated with gangue minerals like magnesite, dolomite, aragonite and calcite. In this study, run of mine ore was subjected to the physicochemical treatment as a function of different size fraction. For observing the wetting behaviour, the contact angle measurements were carried out. It was found that the addition of Na-oleate rendered the particle surface hydrophobic and this finding confirmed the adsorption capability of this collector on the powdered sample. Flotation results indicated that the grade of huntite and hydromagnesite increased from 50% to 84% by decreasing the particle size of the mineral powder. The optimum degree of liberation was achieved at 38 μm. X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were used to perform the phase analysis, surface morphology and elemental analysis of the mineral.

1. Introduction

In recent years, due to the worldwide demand for high-tech materials, the performance requirements in the polymer systems have become more stringent. Especially, flammability of those materials can be considered as a primary problem in this area. Manufacturers and consumers pay serious attention to the flammability properties of polymeric materials not because of the rapid expansion in the utilisation of synthetic materials, but mainly because of the involvement of governments in establishing flammability standards [1,2]. In this manner, the treatment of the high-tech composites with varying application of chemical substances has been known for a long time as reducing the fire hazard of materials in their daily application. The most commonly preferred substances can be counted as fillers. Fillers are classified into 3 groups; inorganic-type fillers, non-combustible thermostable organic fillers and modified organic fillers. Fillers can be dispersed with granular particles (sand, chalk, kaolin, etc.), flaked particles (graphite, mica, talc, etc.) or fibrous particles (glass fibre, asbestos, etc.) or porous particles (glass microspheres, vermiculite, perlite, etc.). In the majority of cases, the inorganic fillers are used [3]. They conserve the structure of polymers by preventing oxygen interaction to the burning polymer or by 'poisoning' the flames. Alum, antimony trioxide, borax, chalk, magnesium oxide or silica are examples of those flame retardant materials.

In our previous works [4,5], huntite and hydromagnesite minerals were investigated in the polymeric composites as prospering flame retardant filler (Fig. 1). A big contribution was provided by the flame retardant property of the composites. It was determined that fire resistivity improvement was possible in two ways; either filler loading amount must be increased or high quality minerals must be utilized. However, using high amount of mineral deteriorated the mechanical properties of the composite product. Hence, it is required to use high quality (free of impurities) minerals. In this study, the purity of the natural additive was tried to be enhanced for the purpose of providing high-quality to the end-product. It enriched the grade of the mineral and eliminated the impurities by the help of the beneficiation techniques.

Beneficiation is the process of separating commercially valuable minerals from their ores. It is required to adequately liberate the desired phases and least adversely affect their purity. It can allow economic recovery of valuable metals from much lower grade ore than before. Flotation is one of the methods used for this purpose.

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Fig. 1. Appearance of huntite and hydromagnesite quarry in Turkey.

It can be defined simply as a process, which selectively separates hydrophobic materials from hydrophilic. Valuable minerals are separated from worthless material or other valuable minerals by inducing them gather in and on the surface of a froth layer. This process is based on the ability of certain chemicals to modify the surface properties of the minerals. Other chemicals are used to generate the froth and others are used to adjust pH. Certain chemicals are even capable of depressing the flotation of minerals that are either to be recovered at a later time or not to be recovered [6,7].

Flotation actually is a process where a particle attaches to air bubble and the elevation of the resulting aggregate particle–bubble to the surface of the aqueous solution with higher density than the resulting aggregate. The binding capacity of the mineral particles to the air bubble depends on the wettability of the mineral surface. Only a particle hardly wettable with water is attached to a gas bubble in contrast to a hydrophilic particle. Therefore wetting property of the mineral is important in the flotation process. Namely, it can be an indicator for the material's hydrophilicity. If a material is hydrophilic, it will float on the fluid surface and can be removed as flotation product or vise verca. This behaviour can be evaluated by contact angle measurement. It is an important criterion for determining the degree of flotation of mineral particles as the primary data. It depends on the strength of adhesion to the bubble, and indicates the degree of wetting when a solid and liquid interact. Small contact angles (90°) correspond to high wettability, while large contact angles (90°) correspond to low wettability [8,9].

Many inorganic substances are hydrophilic. Sulfur, talc and teflon are considered to be highly hydrophobic substances [10]. Hydrophobic substances are usually organic compounds, especially crude oil and its derivatives [11]. In fact contact angle and the wetting behaviour of solid particles are influenced by many physical and chemical factors such as surface roughness and heterogeneity as well as particle shape and size [12]. There is a lack of study regarding the wetting behaviour and contact angle on huntite and hydromagnesite minerals and hence their implication for flotation process. This complementary study will be essential to establish the link between the contact angle and practice of huntite and hydromagnesite in flotation.

Prior to flotation method, a combination of comminution techniques were performed to reduce the raw material to the required product size. Thus some extent mineral impurities can be liberated from the matrix. After the comminution steps, minerals having different particle size were subjected to surface treatment with different chemicals. Furthermore, together with the contact angles measurements, XRD and SEM-EDS analysis were performed to investigate the material structure and morphology. Flotation technique was performed to increase the huntite and hydromagnesite grade in the material.

2. Materials and methods

The material was received from Isparta region in Turkey. Mixed and a well representative sample was drawn in each case for detailed characterisation and beneficiation studies. After crushing and grinding steps, the material was sieved to be separated into different size. Four narrow sieved fractions of the material were used; sieved fractions (μm): +212 ($x > 212$), −212+180 ($212 \geq x > 180$), −180+106 ($180 \geq x > 106$), −106+75 ($106 \geq x > 75$), −75+38 ($75 \geq x > 38$), −38 ($38 \geq x$). Before sieving, the sieves were weighed and stacked up, with the smallest one at the bottom and the largest one at the top (sieves with mesh openings of 38, 75, 106, 180 and 212 μm). A pan was placed underneath the sieves to collect the particles, which passed through all sieves. The powder was loaded onto the top screen, and this sieve was closed with a solid cover. Sieving was performed on 100 g sample, the job was repeated until obtaining 50 g each of fractions. 50 g material feed is required in the flotation process.

X-ray diffraction studies were carried out for the identification of mineral phases present with an X-Ray Diffractometer Rigaku SmartLab. SEM micrographs and EDS analysis were taken with JEOL JSM-7600F. Related with the contact angle measurements, different sizes of mineral powders were molded with 3 tons of pressure using a molding machine for preparation of the specimens. Each specimen has 10 mm diameter. After grinding with series of silicon carbide papers, the specimen surfaces were polished with chromium oxide powder, aluminium oxide powder, and diamond paste, respectively. In all cases when passing from one step to the next, the surfaces of the samples were washed with water. After drying at 106 °C, wetting properties were estimated. There are several methods, captive bubble, sessile drop, tilting drop, pendant drop, receding contact angle etc., can be used for the wetting property observation. Ideally, regardless of the type of the methods used, similar results should be obtained in all studies [13]. In this study, a special arrangement for measuring the contact angle was made by means of captive bubble method. In this method, instead of placing a drop on the solid, a bubble of air is injected from beneath to a solid. The bubble is located surface to the in the liquid (Fig. 2). The experimental contact angle meter, Goniometer, setup used for this purpose is given in Fig. 3. Contact angle

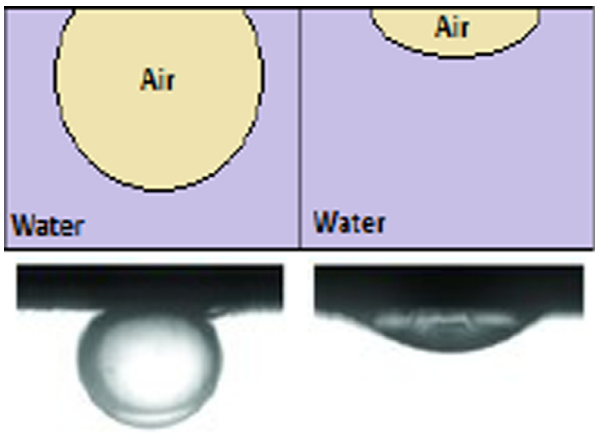


Fig. 2. Schematic captive bubbles.

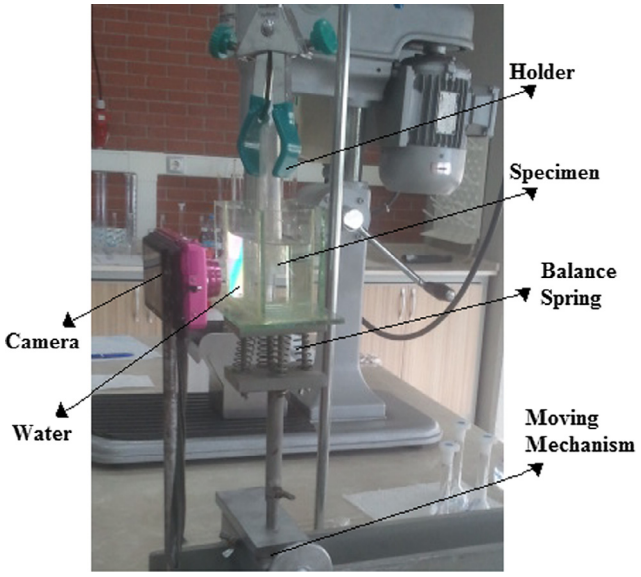


Fig. 3. Contact angle goniometer.

Table 1
Optimum conditioning parameters for flotation.

pH	Natural
Powder size distribution	−38, −75+38, −106+75, −180+106, −212+180, +212
Collector	Na-Oleate, 2000 g/t
Frother	MIBC, 30 g/t
Na-Oleat conditioning time	3 min
Conditioning time with frother	1 min
Rotor speed	1100 rpm

measurement was performed in pure water and Na-Oleate including water, respectively. Note that the size of the bubble should be small enough so that the effect of gravity is eliminated, as it was shown in earlier studies by Tadmor [14].

Regarding the beneficiation process, flotation method was applied by using Denver type flotation machine with one-litre capacity. It was carried out after conditioning the sample with a required amount of reagents for a predetermined time. Na-Oleate was used as a collector. The agitation intensity, the pulp density, and pH were controlled during the experiments. All the flotation tests were carried out at a fixed pulp density. The concentrates and tailings were collected separately, dried, weighed and analysed for different constituents to assess the product quality. Table 1 depicts the experiment conditions.

To evaluate the flotation products, the quantitative phase analysis was carried out via Rietveld Refinement Technique. The intensity at a given step in XRD-pattern is determined by summing the contributions from the background and all neighbouring Bragg reflections as follows (Eq. (1)) [15]:

$$y_i(c) = S\sum_k p_k L_k |F_k|^2 G(\Delta\theta_{ik}) P_k + y_{ib}(c) \quad (1)$$

where S is the scale factor, L_k is the Lorentz and polarization factors for the kth Bragg reflection, F_k is the structure factor, p_K is the multiplicity factor, P_k is the preferred orientation function $G(\Delta\theta_{ik})$ is the reflection profile function, θ_k is the Bragg angle for the kth reflection, and $y_{ib}(c)$ is the background [15]. Considering the equation and the intensity values of the peaks, the estimated intensities were fitted to the observed intensities in the pattern. Following this process, the contribution of each mineral phase to the related intensities was calculated. Based on these contributions, the quantitative phase distribution of each sample was determined.

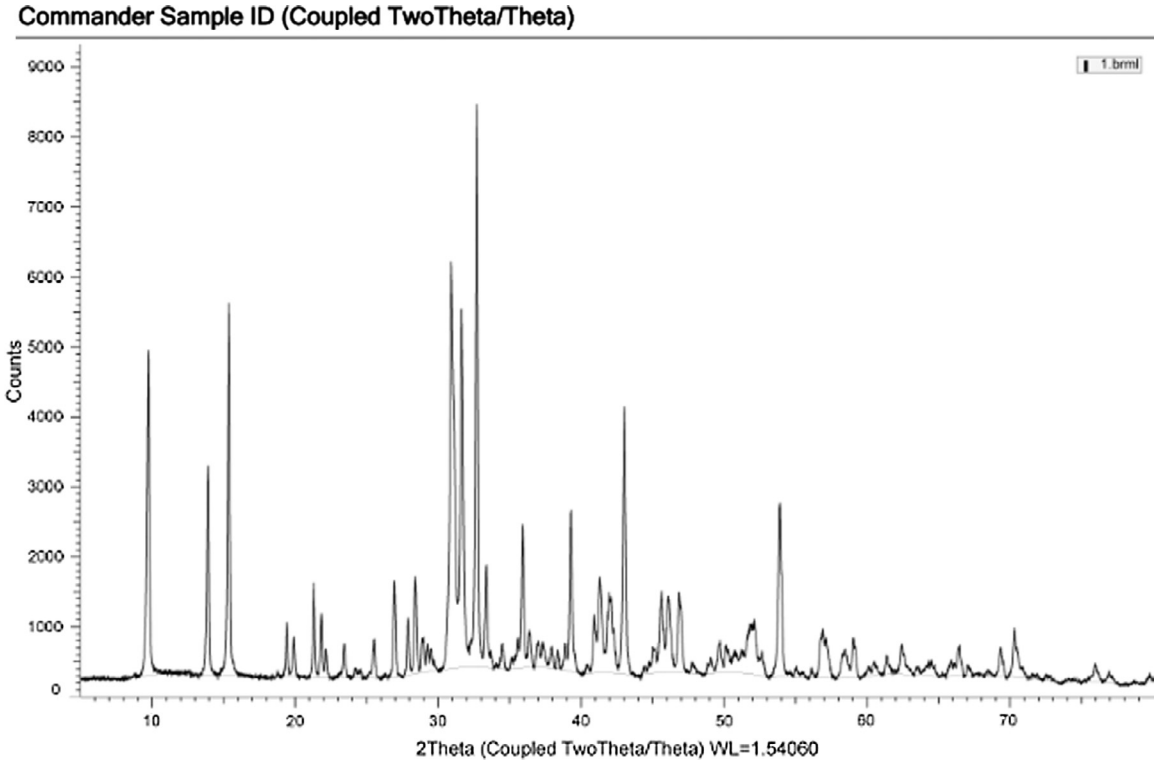


Fig. 4. XRD analysis of as-received huntite and hydromagnesite.

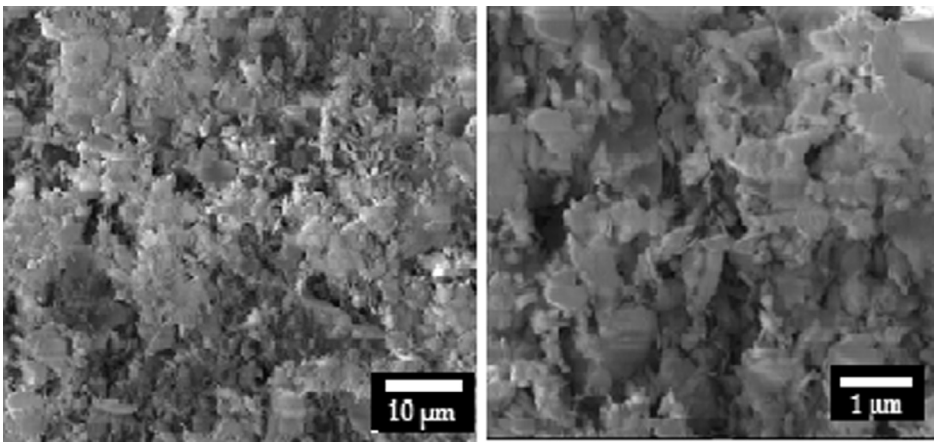


Fig. 5. SEM micrographs of as-received huntite and hydromagnesite.

3. Results and discussions

XRD analysis of the received huntite and hydromagnesite is shown in Fig. 4. It is found from this result that the basic minerals are hydromagnesite ($Mg(CO_3)_3{\cdot}3H_2O$) and huntite ($Mg_3Ca(CO_3)$). Magnesite exists as the main impurity in the ore. And the other impurities can be counted dolomite and calcite. The main phases with high intensity are huntite and hydromagnesite. The analysis result supports Kirschbaum's studies [16] in which he stated the impurities magnesite, aragonite, and calcite phases which are accompanying with huntite and hydromagnesite [17,18].

Fig. 5 demonstrates SEM micrographs, and EDS analysis of huntite/hydromagnesite mineral particles are shown in Fig. 6. It is clearly seen that the mineral particles are not circular but they are lateral with irregular shapes. EDS analysis supports XRD result as in the elemental analysis the elements of Mg, Ca, C, and O were indicated. There seem no other elements as impurity [18].

The determined contact angle is demonstrated at the graph in Fig. 7. According to this graph, the minimum value of the angle is

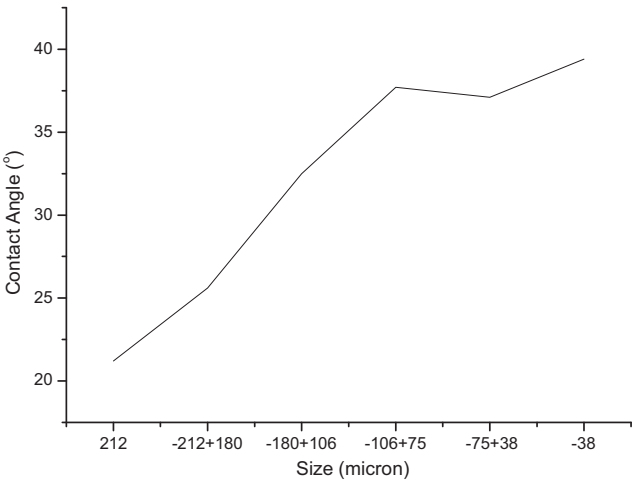
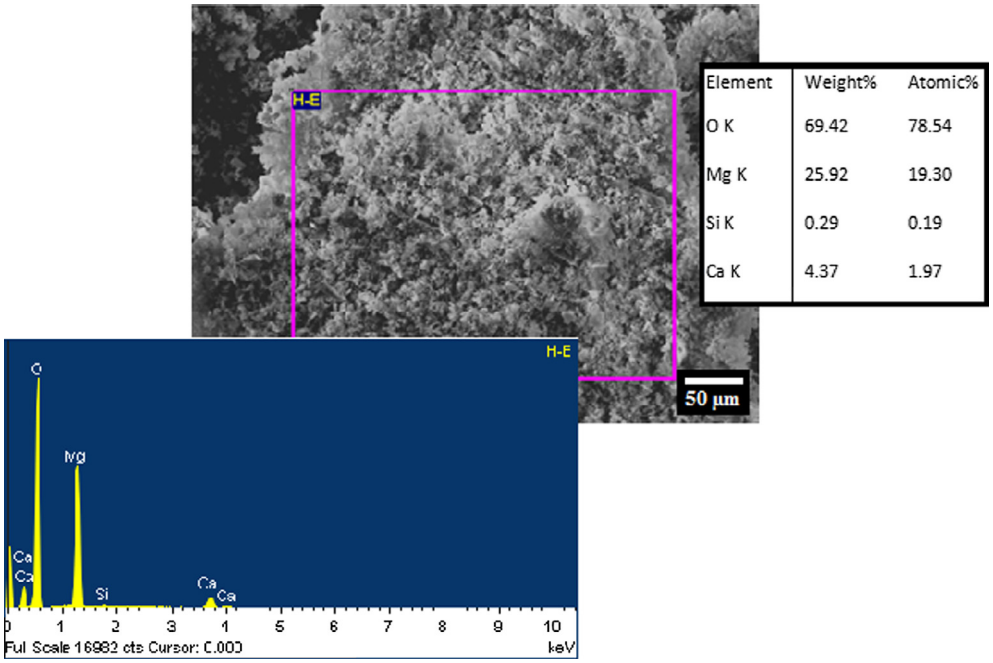


Fig. 7. Contact angle measurements according to particle size distribution.



Element	Weight%	Atomic%
O K	69.42	78.54
Mg K	25.92	19.30
Si K	0.29	0.19
Ca K	4.37	1.97

Fig. 6. EDS analysis of as-received huntite and hydromagnesite.

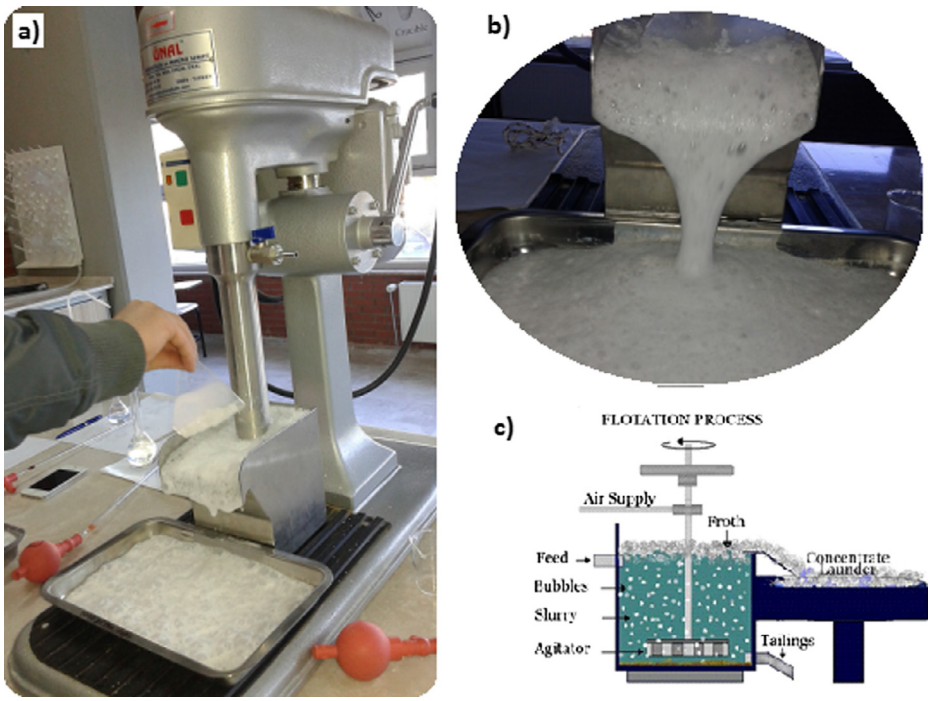


Fig. 8. (a and b) Flotation performance, (c) Schematic illustration of flotation.

Table 2
Huntite and hydromagnesite flotation results; concentrate, tailing and recovery.

Size (μm)	Concentrate (g)	Tailing (g)	Recovery (%)
+212	13.87	36.13	27.74
−212+180	17.83	32.17	35.66
−180+106	18.26	31.74	36.52
−106+75	20.59	29.41	41.18
−75+38	19.68	30.32	39.36
−38	29.16	20.84	58.32

measured as 21.2° degree in the coarser material. And, the maximum value of the contact angle was reached 39.4° degree at (−) 38 μm mineral. It can be easily seen that the decreasing the particle size increased contact angle, i.e. hydrophobic property was increased. This will support the flotation recovery results as discussed in the progressive sections.

In Fig. 8, flotation experiment and the principle are demonstrated. In the experiment, the beneficiation performance was evaluated according to the particle distribution of the flotation feed. Table 2 depicts the experiment results by means of concentrate, tailing and flotation efficiency. Very successful performance was achieved. It can be easily seen from the Figure that decreasing the particle size increased the quantity of the minerals in the froth. Concentrate amount was 13.87 g by using the coarser material, but it was increased to 29.16 g by using −38 μm mineral. Accordingly, recovery increased from 27.74% to 58.32%. The reason for this may be increasing the surface area and degree of liberation as mentioned previously [19,20].

For the analyzing of the flotation products, quantitative analysis was done to all concentrate materials (Fig. 9). The results are demonstrated in Table 3. It shows the percentage of huntite-hydromagnesite and magnesite quantity in the concentrate by weight percent. In this evaluation, similar results were obtained. Indeed, the concentrate of the first flotation experiment (+212 μm) has 72.30% huntite and hydromagnesite and 27.70% magnesite. However, in the last experiment (−38 μm) huntite

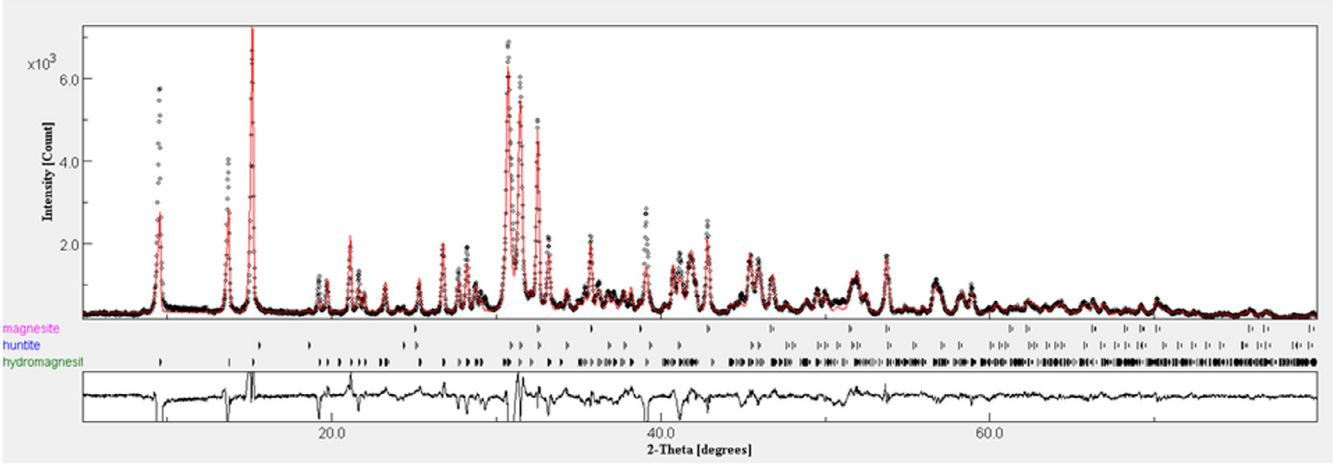


Fig. 9. Semi-Quantitative XRD analysis of concentrate.

Table 3
The quantitative phase analysis results of flotation products (float).

Size (μm)	Huntite + Hydromagnesite (%)	Magnesite (%)
+212	72.30	27.70
−212+180	73.80	26.20
−180+106	84.10	15.90
−106+75	74.10	25.90
−75+38	81.45	18.55
−38	84.30	15.70

and hydromagnesite has increased to 84.30% and the magnesite has decreased to 15.70%.

The results show that particle size is an important factor in the flotation process. It can be said that decreasing the size of huntite and hydromagnesite mineral particle increased the float amount in the flotation process. There has been no any study regarding size effect in huntite and hydromagnesite flotation, however, it is rare for other minerals. For instance, Qu et al. [21] investigated flotation characteristics and particle size distribution of micro-fine low-rank coal. They claimed that the dominant size fraction of the low rank raw coal was −0.045 mm size fraction with a yield of 91.65% and ash content of 46.25%. The concentrate contained 83.38% of −0.045 mm size fraction with an ash content of 24.98%. Li et al. [22] studied this topic for the coal flotation and they found that the best flotation selectivity was obtained from the middle size fraction, 0.250+0.075 mm, while the selectivity of −0.500+0.250 and −0.075 mm particles was decreased. Xia et al. [23] showed that a better particle size for the flotation of heavily oxidized coal ranged from 11 to 74 μm. For the coal maceral group's separation using flotation, the vitrinite was mainly concentrated in the fine size fractions (−40+25 and −25 μm). As it can be seen, studies have found different results for better recovery, although in our work better performance has been obtained with finer fractions. The important thing is to perform this checkup in order to increase the performance and decrease the losses.

On the other hand, the results give an idea about the surface-collector interaction that can be explained by the zeta potential differences on the surface of huntite, hydromagnesite and the impurities [24,25]. This experiment observed that the surface charges of huntite and hydromagnesite are very similar in the presence of Na-Oleate. However, there could be obtaining a slight difference on the surface charges of magnesite.

To summarize, all above results depict that in the solids separation -flotation- techniques, success depends on the use of the variety of reagents, controlling the wetting behaviour of solid surfaces and particle dispersion. Obtained results of this study give useful data to other researchers to separate the Mg-rich carbonate minerals from each other and to investigate other usage areas. Furthermore, it is an unquestionable contribution to the economy of a country of the added value of high-grade products as a result of the enrichment material which is still processed in the crushing-grinding plant to be marketed directly.

4. Conclusion

Beneficiation performance of huntite and hydromagnesite was investigated by using different size of minerals and with surface treatments. To examine the wetting property, the contact angle measurements were carried out according to the particle distribution and overarching of this to beneficiation of the minerals. The results showed that decreasing the particle size increased contact angle and the hydrophobic property was increased. Froth flotation technique was very successful to increase the flame retardant huntite and hydromagnesite grade from 50% to 84% with −38 μm mineral particle size. XRD and SEM analyses were also used to evaluate the phase and the morphology of the materials. With the help of the data obtained in this work, it can be possible to go into production in never made production areas with low grade and impurity. Furthermore, those high-grade products will be a quite high contribution to the economies of the countries.

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