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Article

The beneficiation of the Pütürge pyrophyllite ore by flotation: mineralogical and chemical evaluation

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Abstract

Samples from the pyrophyllite reserves in the Malatya–Pütürge region, used in the production of the whitest cement in Europe, were beneficiated using flotation. The mineralogical composition of the natural pyrophyllite, as determined using X-ray diffraction, includes pyrophyllite, kaolinite, quartz, illite–mica and feldspar. The chemical composition of pyrophyllite contains 69.75% SiO_2 and 23.04% Al_2O_3. The pyrophyllite percentage (40–45 wt.%) of the natural sample increased to 60–80 wt.% after flotation. In flotation experiments, the effects of reagent amounts, types and their mixtures were investigated. Methyl isobutyl carbinol (MIBC) and pine oil as frothers and kerosene as a collector were used in the flotation studies. The use of reagents as mixtures has a positive effect on the beneficiation compared to use on their own. The best result was obtained for a mixture of MIBC with kerosene, which is a non-ionic hydrocarbon oil, yielding a concentrate containing 26.63% Al_2O_3. Improved results were also observed for kerosene plus frother mixtures after flotation cleaning circuits. The bubbles formed during flotation were photographed and the bubble diameters were measured using the *ImageJ* program. The Al_2O_3 content was evaluated by correlating the bubble diameters. In general, selectivity decreased during experiments in which bubble diameters were reduced.

Keywords: flotation, frothers, Pütürge, pyrophyllite, XRD

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Phyllosilicate minerals are common hydrophobic minerals present as impurities in complex sulfide ores and include aluminium silicate minerals such as pyrophyllite, kaolinite, muscovite and chlorite, as well as the corresponding magnesium silicate minerals, talc, serpentine and phlogopite (Du & Miller, 2007). Theoretically, pyrophyllite ($Al_4Si_8O_{20}(OH)_4$) is composed of 66.65% SiO_2, 28.35% Al_2O_3 and 5.00% H_2O, and it is a dioctahedral 2:1 clay mineral consisting of an octahedral aluminium oxyhydroxide sheet sandwiched between two tetrahedral sheets (Bentayeb *et al.*, 2003; Deer *et al.*, 2013).

Pyrophyllite occurrences are divided into two general groups: pyrophyllites formed by the hydrothermal alteration of acidic volcanics and pyrophyllites of metamorphic origin. Pyrophyllite is associated generally with minerals such as kaolinite, quartz, feldspar, sericite, diaspore, kyanite, andalusite, chloritoid, chlorite, epidote and rutile in these formations (Cornish, 1983; Harben & Kuzvart, 1997; Harben, 1999; Hida & Kitagawa, 2006; Virta, 2009; Madejová *et al.*, 2017). Pyrophyllite formations of various mineralogical compositions are known by names such as 'roseki', 'agalmatolite' and 'wonderstone' in various countries (Harben, 1999).

High-quality pyrophyllite is used in the refractory, ceramic, fibreglass, pesticide, fertilizer, paper, paint, plastic, rubber, cement, building material and pharmaceutical industries. However, impurities in pyrophyllite ores limit their use and therefore the beneficiation of some ores with small pyrophyllite contents is necessary (Evans & Guggenheim, 1988; Harben, 1999; Jena *et al.*, 2015; Zelazny & White, 2018). The pyrophyllite contents in ores determine the areas of use of pyrophyllite in industry by determining the refractory properties, coefficient of thermal expansion, hardness and colour (Ciullo, 1996; Jeong *et al.*, 2017). The quality of pyrophyllite is affected adversely by undesirable elements such as Fe, Ti, alkali ions and gangue minerals such as quartz, feldspar, mica and rutile (Harvey & Murray, 1997; Hida & Kitagawa, 2006; Jeong *et al.*, 2017; Kim *et al.*, 2019; Ali *et al.*, 2021). On the other hand, pyrophyllite can be used as a substitute for kaolinite in many industrial applications such as the ceramic, pottery and filling industries, and it can also be used as a substitute for talc in many applications, especially as a filler pharmaceutical, and in medical applications (Mukhopadhyay *et al.*, 2010; Ali *et al.*, 2021).

Various methods have been tested for removing impurities from non-metallic minerals. In the case of pyrophyllite, wet processing methods have been explored, such as flotation, gravity separation, leaching, microwave treatment and magnetic separation (Birinci & Sarıkaya, 2004; Bozkaya *et al.*, 2007; Bulatovic, 2007; Perepelitsyn *et al.*, 2008; Xia *et al.*, 2009; Abdrakhimova, 2010; Jena *et al.*, 2015; Cho *et al.*, 2016; Kim *et al.*, 2019). Pyrophyllite does not have a layer charge because only Si^{4+} occupies the tetrahedral sites and two-thirds of the octahedral sites are filled with Al^{3+} only. The electrically neutral sheets in pyrophyllite are bonded together by relatively weak dipolar and van der Waals forces (Evans & Guggenheim, 1988). Due to this weak interlayer

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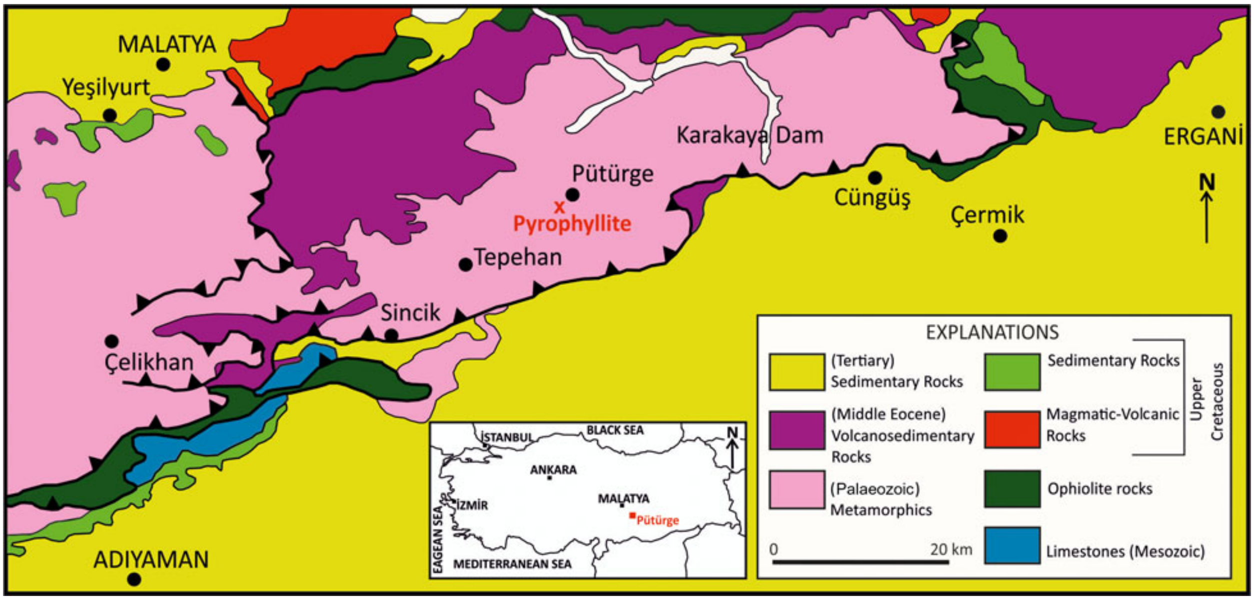

Fig. 1. Location and general geological map of the Malatya–Pütürge region in the Southeast Anatolian Belt (MTA, 2002).

bonding force, the pyrophyllite surface is electrically neutral, which gives rise to natural floatability. Therefore, pyrophyllite is a fast-floating and easy-sliming mineral (Erdemoğlu & Sarıkaya, 2002; Das & Mohanty, 2009; Zhao *et al.*, 2017).

The faces of pyrophyllite are naturally hydrophobic; however, the edges of the pyrophyllite particles break the Si–O or Al–O bonds and consequently are hydrophilic (Miller *et al.*, 2007). The ratio of hydrophilic/hydrophobic surface sites is expected to affect the electrokinetic properties and the flotation behaviour of this mineral. The point of zero charge for pyrophyllite is reported as pH 2.4 (Hu *et al.*, 2003). Liu & Bai (2006) showed that surface ζ-potential variations as a function of pH show similar trends in various pyrophyllite samples. While the isoelectric point of various samples varies from 2.35 to 3.46, the isoelectric point shows a negative correlation with the mass fractions of SiO_2 and Na_2O. Pyrophyllite reduction is important because in many cases pyrophyllite is considered to be a gangue mineral in flotation separation. Polysaccharides such as guar gum have been studied as pyrophyllite reducers (Zhao *et al.*, 2017, 2019a, 2019b, 2019c).

Frothers are surface-active chemicals that concentrate at the air–water interface. They prevent air bubbles from coalescing or bursting by lowering the surface tension of a slurry. Frothing properties can be persistent or non-persistent depending on the desired stability of the froth (Laskowski *et al.*, 2003; Laskowski, 2004; Melo & Laskowski, 2006; Bulatovic, 2007; Finch *et al.*, 2008; Atak, 2017). Frothers are very effective for the flotation of naturally floating minerals (Gupra *et al.*, 2007; Khoshdast & Sam, 2011). Previous studies have assessed the effects of frother blends on flotation (Elmahdy & Finch, 2013; Ngorama *et al.*, 2013; Dey *et al.*, 2014; McFadzean *et al.*, 2016; Bayram *et al.*, 2018). The aim of this study is to investigate the effects of frothers and mixtures of frothers with kerosene on pyrophyllite flotation. The effect of bubble size on flotation was tested by measuring the bubble diameter during the experiments. This study also aimed to obtain optimal outcomes by controlling the flotation steps mineralogically and chemically.

Materials and methods

The pyrophyllite material used in this study was collected from the quarries of the Çimsa Company in the Pütürge region (Malatya, Turkey). The Pütürge metamorphic massif, located in eastern Turkey, is one of the two metamorphic massifs on the Bitlis–Pütürge Suture Zone (Southeast Anatolian Belt), which is the collision zone of the Arabian and Anatolian plates. The metamorphics (Palaeozoic) of the Pütürge massif constitute the basement in the region. An ophiolitic mélange and ophiolitic olistostrome group rocks (Mesozoic) are located in the Bitlis–Pütürge Suture Zone (Yazgan & Chessex, 1991; Dolmaz *et al.*, 2009), followed by Upper Cretaceous magmatic and sedimentary rocks and Tertiary sedimentary (mainly carbonates) and volcanosedimentary rocks (Fig. 1; MTA, 2002).

The pyrophyllite rocks related to the gneiss and mica schists of the Pütürge metamorphic massif consist mainly of pyrophyllite, kaolinite (plus dickite), quartz and muscovite and minor amounts of kyanite, sericite, illite and alunite (Uygun & Solakoğlu, 2002; Erdemoğlu *et al.*, 2020). Pütürge pyrophyllite with small iron and chromium contents has a bright white colour after firing, and it is has been used in white cement production, where it is known to produce the whitest cement in Europe (Uygun & Solakoğlu, 2002). There are ~6 million tons of apparent pyrophyllite reserves in the region (Aras *et al.*, 1993).

The mineralogical compositions of the natural pyrophyllite (NP) sample and final concentrate (FC) samples obtained after flotation experiments were identified using X-ray diffraction (XRD) at the Istanbul Technical University using a Bruker D8 Advance instrument with Ni-filtered Cu-$K\alpha$ radiation in the 2–70°2θ range at 1° min^{-1} cm^{-1} scanning speed, 40 kV tube voltage and 40 mA current. The semi-quantitative mineralogical compositions of the natural and experimented pyrophyllite samples were estimated using the XRD reference intensity method (wt.%; Chung, 1975). The heights of the most intense peaks and the reference intensity ratios (RIRs) of kaolinite, feldspar, quartz, illite and mica were used for the calibrations (Bulut *et al.*, 2009; Ekinci-Şans *et al.*, 2015). The kaolinite RIR was also adopted for pyrophyllite. Considering the margin of error of the method,

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Table 1. Flotation experiment conditions.

Condition	Value
Conditioning time	5 min
Flotation time	6 min
Stirring speed	1200 rpm
Cell volume	1.5 L
Sample amount	300 g
pH (natural pH of the sample)	8.0–8.5

the error in terms of mineral percentage is ±5%. Additionally, the mineral contents determined using XRD were compared with the chemical composition of the NP sample. Major oxide chemical analyses of the samples were performed at Istanbul Technical University (JAL Laboratory) using X-ray fluorescence with a Bruker S8 Tiger instrument on pressed discs that were prepared using a binder and boric acid.

The pyrophyllite sample, with an average size of ~20 mm, was first fed into a jaw crusher and the particle size reduced to <6 mm. Subsequently, the sample was fed into a roller crusher and its particle size was reduced to <1 mm. The wet grinding method in a ceramic mill (diameter: 17 cm; length: 21.5 cm; ball size: 1.8 cm) was used for size reduction. In the grinding process, the solid ratio in pulp was adjusted to 60% and the ball mill charge was 40%. The rotation speed of the ball mill was 80 rpm. Particle-size analyses of the samples with reduced particle sizes were performed using a Malvern Mastersizer 3000 particle-size analyser. For particle-size analysis, the samples were prepared as homogenous suspensions with water (2% solid ratio), which were fed into the device at a concentration sufficient for analysis. The particle-size analysis was performed in triplicate.

In the flotation experiments, two frothers and their mixtures with kerosene were investigated. Methyl isobutyl carbinol (MIBC), pine oil (terpineol) and kerosene (non-ionic collector) reagents were used in the flotation studies. Detailed experiments were carried out depending on the amount of reagents. In this study, only the experimental results that are important in terms of content and distributions have been selected and examined. All flotation experiments were carried out with 300 g of sample using a Denver flotation machine. A pulp ratio of 20% solids in a cell volume of 1.5 L was used. The flotation conditions are listed in Table 1. A flow diagram of the size-reduction and flotation experiments is given in Fig. 2. In the flotation experiments, the bubbles formed at the beginning of the flotation process and at the end of the 5 min conditioning period were photographed from the same angle. A measuring unit was placed at the edge of the cell. Then, bubble diameters were determined as Feret diameters using the *ImageJ* program. Large numbers of bubble diameters were measured to reduce deviation and to achieve accurate results. The Al_2O_3 content and recoveries were evaluated by correlating the bubble diameters. The bubble-diameter measurement method and the images taken during the experiment are shown in Fig. 3, and some photographs of bubbles on flotation cells with various reagents are shown in Fig. 4.

Results

Natural pyrophyllite

The Pütürge NP sample contains abundant pyrophyllite, quartz, kaolinite and smaller or trace amounts of illite–mica and feldspar (Fig. 5). The crystalline phases were identified using mineral cards given in JCPDS (1974) (pyrophyllite: 2-613 and 12-203; quartz: 5-490; kaolinite: 14-164; illite–mica: 9-343 and 7-42; and feldspar–microcline: 19-932). From the XRD modal analysis results and chemical compositions, the mineral abundances (wt.%) of the NP sample were pyrophyllite (40–45%), kaolinite (20–25%), quartz (20–25%), illite–mica (10–15%) and feldspar (<5%).

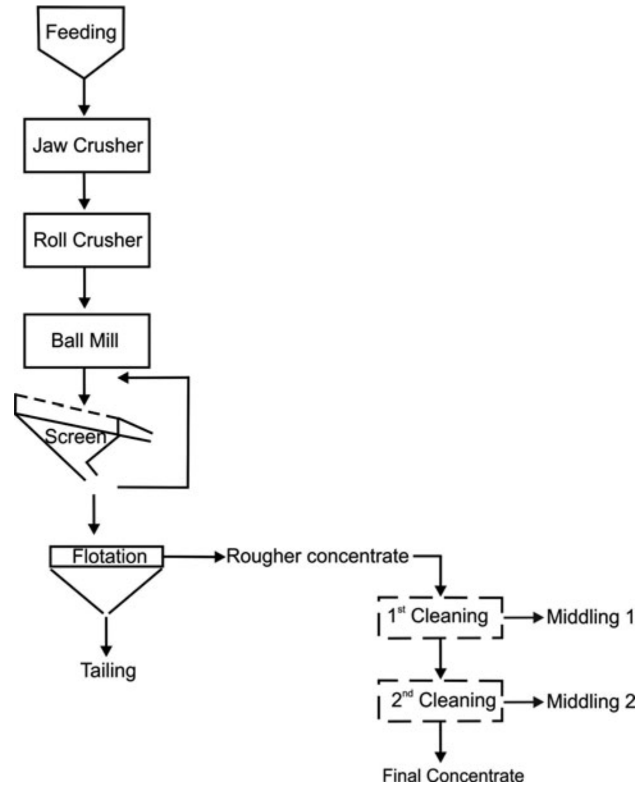

Fig. 2. Flow diagram of the size reduction and flotation experiments on the ore sample (dashed lines indicate circuits that were implemented only in some situations).

The spacing values of the basal distances (d_{002}, d_{004}, d_{006}, d_{008} and $d_{00,10}$) of the Pütürge pyrophyllite were 9.19, 4.59, 3.06, 2.28 and 1.83 Å, respectively (Table 2). Table 1 also lists the XRD data of the basal series for two pyrophyllites from the USA (card no. 2-613) and Japan (card no. 12-203) given in JCPDS (1974) with the Pütürge pyrophyllite. According to the XRD data, the most intense peaks of pyrophyllites are at 9.19, 4.59 and 3.06 Å, and these were used to interpret the flotation results. The most intense peaks were 7.16 and 3.58 Å (d_{001} and d_{002}) for kaolinite, 9.97 and 4.99 Å for illite–mica (d_{002} and d_{004} for illite; d_{003} and d_{006} for mica) and 3.24 Å for feldspar–microcline (Fig. 5).

The chemical composition of the NP sample was in accord with the mineralogical composition. The SiO_2 (69.75%) is due to quartz, pyrophyllite and kaolinite, and the Al_2O_3 (23.04%) is due to pyrophyllite and kaolinite. Some of the SiO_2 and Al_2O_3 contents are associated with feldspar. The K_2O (1.02%), CaO (0.74%), Na_2O (0.18%) and MgO (0.12%) contents are attributed to illite–mica, feldspar and probably pyrophyllite and/or kaolinite. The NP sample also contains 0.23% Fe_2O_3, 0.32% TiO_2 and 4.60% loss on ignition (LOI). The particle-size analysis results for the NP sample are shown in Fig. 6. Approximately 90% of the material is <23.7 μm in size.

Flotation experiments

Single use of frothers

Flotation experiments were carried out with two different frothers at two different concentrations. Table 3 shows the effects of the

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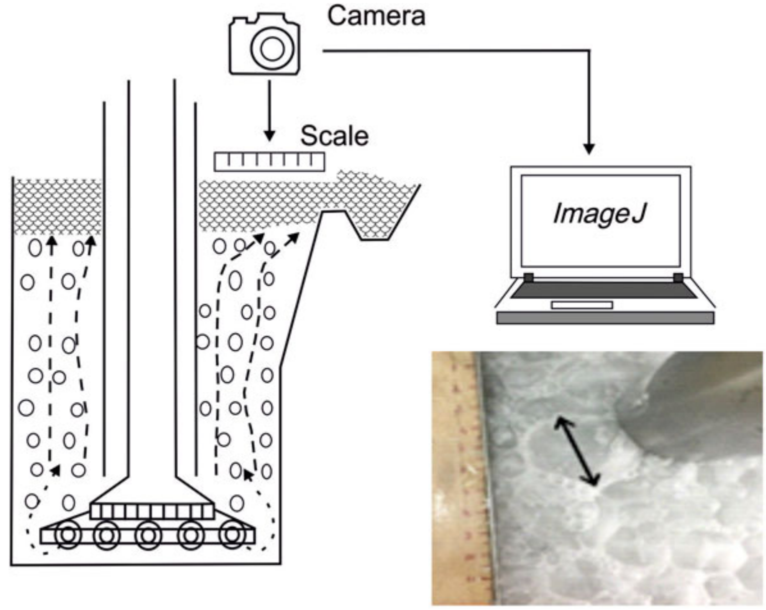

Fig. 3. Measurements of bubble diameters and an image of the bubbles during flotation.

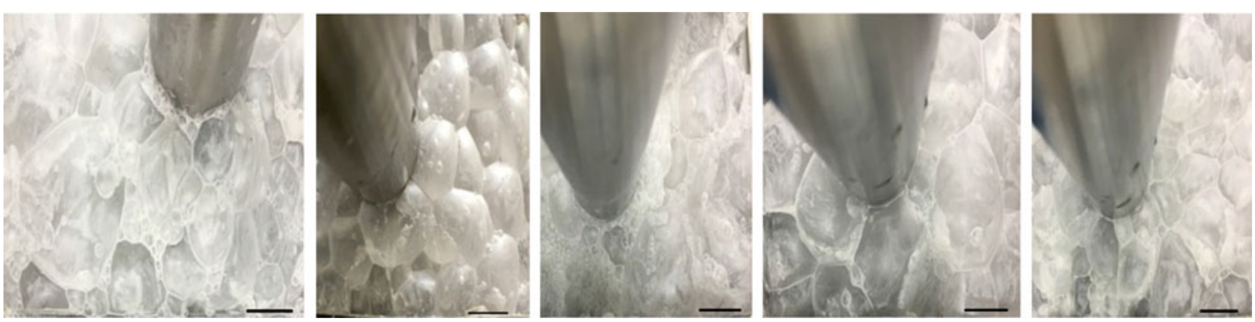

Fig. 4. Photographs of bubbles on flotation cells with various reagents. From left to right: 150 g t^{-1} MIBC, 150 g t^{-1} pine oil, 150 g t^{-1} kerosene plus MIBC, (150 g t^{-1} kerosene plus pine oil and 550 g t^{-1} kerosene plus MIBC (scale bar = 2 cm).

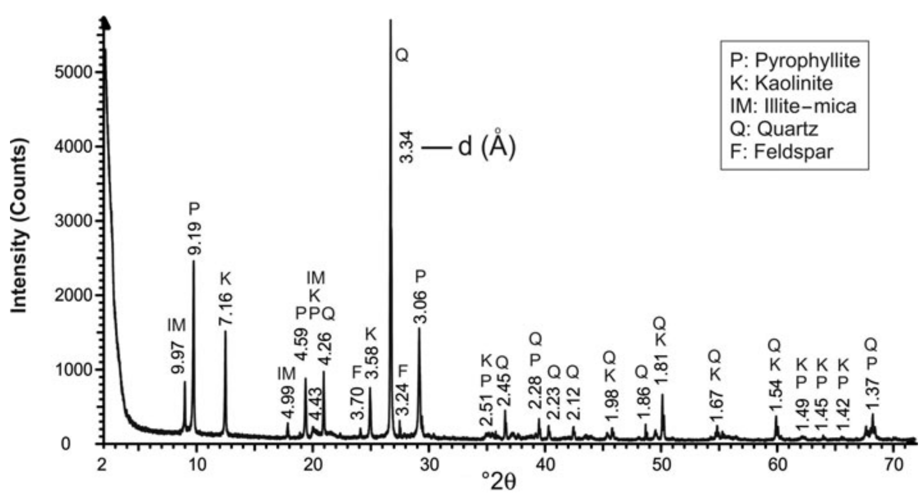

Fig. 5. XRD trace of the Pütürge NP sample.

frothers in their single use on the distributions and contents of SiO_2, Al_2O_3 and LOI. Figure 7 shows the bubble diameters depending on the frother used.

Mixture of frothers with kerosene

Kerosene was mixed with the frothers and the effects of kerosene plus MIBC and kerosene plus pine oil mixtures on flotation were

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Table 2. XRD data of the basal series d_{00l} of two pyrophyllites (card 2-613 for the US pyrophyllite and card 12-203 for the Japanese pyrophyllite; JPDS, 1974) and the Pütürge pyrophyllite.

Miller indices (hkl)	*d* (Å) (RI)		
Pyrophyllite	Mariposa (USA)	Nagano (Japan)	Pütürge (Turkey)
(002)	9.14 (40)	9.21 (60)	9.19 (100)
(004)	4.57 (50)	4.58 (50)	4.59 (34)
(006)	3.04 (100)	3.08 (100)	3.06 (61)
(008)	2.29 (20)	2.31 (6)	2.28 (3)
(00,10)	1.83 (40)	1.84 (6)	1.83 (6)

RI = relative intensity.

investigated. A total of 150 g t^{-1} (75 + 75 g t^{-1}, kerosene + frother) of reagent was used. When pine oil and kerosene were used together, the concentrate content was Al_2O_3 24.08 wt.%, the distribution decreased to 42.63% and the SiO_2 content in the concentrate was ~67 wt.%. The large SiO_2 content in the concentrate indicated that the concentrate was not clean. On the other hand, in the experiment with the kerosene plus MIBC mixture, the Al_2O_3 content of the concentrate was 27.17 wt.% and the distribution was 45.98%. As the concentrate distribution was small, totals of 150 g t^{-1} MIBC and 400 g t^{-1} kerosene were mixed and the experiment was repeated, resulting in a concentrate with 26.63 wt.% Al_2O_3 content and a distribution of 65.91% (Table 4). When the results were compared in terms of bubble diameters, the bubble sizes were almost the same in these experiments. The effects of using the kerosene plus frother mixtures on bubble size are shown in Fig. 8.

Cleaning circuits in flotation

The test concentrates showing the best results were cleaned without the addition of reagent (except in the case of the single use of pine oil). Experiments were conducted with mixtures of kerosene plus MIBC at small and large dosages of 150 g t^{-1} for FC-2 and 550 g t^{-1} for FC-5. In addition, a kerosene plus pine oil mixture of 150 g t^{-1} for FC-1 and single pine oil usages of 150 g t^{-1} for FC-3 and 200 g t^{-1} for FC-4 were examined. The Al_2O_3 contents of the concentrates were large (Table 5). The effects of these cleaning circuits on bubble diameter are shown in Fig. 9. There was no significant difference in the bubble diameters measured in the cleaning circuits when using combinations of various reagents.

Mineralogical and chemical interpretation

The XRD traces of the NP sample and the FC samples (FC-1 to FC-5) are shown in Fig. 10, and the mineral contents of the

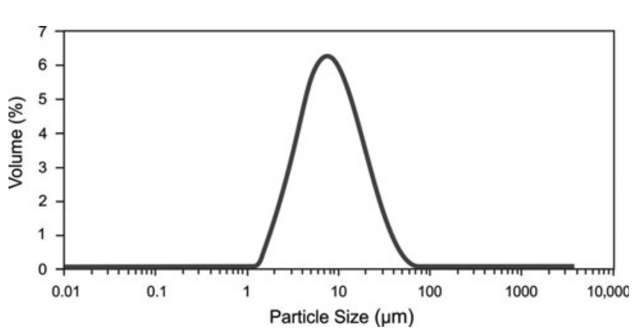

Fig. 6. Particle-size distribution of the NP sample.

Table 3. Single usage of frothers.

Dosage (g t^{-1})	Product	Weight (%)	SiO_2 (%)		Al_2O_3 (%)		LOI (%)	
			Cont.	Distr.	Cont.	Distr.	Cont.	Distr.
150	Concentrate	47.83	66.01	45.75	26.56	53.15	5.32	56.46
MIBC	Tailings	52.17	71.75	54.25	21.46	46.85	3.76	43.54
	Total	100.00	69.00	100.00	23.90	100.00	4.51	100.00
200	Concentrate	47.75	66.27	45.24	25.94	54.11	5.75	57.33
MIBC	Tailings	52.25	73.29	54.76	20.10	45.89	3.91	42.67
	Total	100.00	69.94	100.00	22.89	100.00	4.79	100.00
150	Concentrate	44.63	65.47	41.70	25.97	51.53	6.63	59.09
Pine oil	Tailings	55.37	73.79	58.30	19.69	48.47	3.70	40.91
	Total	100.00	70.08	100.00	22.49	100.00	5.01	100.00
200	Concentrate	50.79	66.26	48.74	25.32	56.25	6.28	57.97
Pine oil	Tailings	49.21	71.91	51.26	20.32	43.75	4.70	42.03
	Total	100.00	69.04	100.00	22.86	100.00	5.50	100.00

Cont. = content, Distr. = distribution.

samples estimated using quantitative XRD analysis are given in Table 6. Mineral percentages have been presented in 5% intervals (97.5–102.5% in total). The differences between the NP and FC samples were detected using the most intense peaks for each mineral (pyrophyllite: 9.19, 4.59 and 3.06 Å; kaolinite: 7.16 and 3.58 Å; quartz: 3.34 Å; illite–mica: 9.97 Å; feldspar: 3.24 Å).

The pyrophyllite and kaolinite contents increased and the quartz, illite–mica and feldspar contents decreased in the FC samples compared to the NP sample (Fig. 10). Hence, flotation appears to be a successful separation method in the light of these XRD results (Table 6). All FC samples were enriched in pyrophyllite (from 40–45% in the NP sample to 60–80% in the FC samples; Table 6). The greatest increases in pyrophyllite percentages were in samples FC-2 (75–80%) and FC-1 (70–75%). The kaolinite content remained unaffected (20–25% in the NP sample and 15–30% in the FC samples). The kaolinite content decreased slightly in FC-2 and increased in FC-3, FC-4 and FC-5.

Regardless of the reagent used, the quartz, illite–mica and feldspar contents were reduced or disappeared in the flotation products. Quartz was reduced greatly (to <10%), feldspar disappeared and mica remained in trace amounts (<2%) in the FC samples (Table 6). Thus, the total abundances these three minerals (quartz, feldspar and illite–mica) decreased from 35–40% in the NP sample to <10% in the concentrated products (Table 6). In terms of quartz, the FC-1 concentrate that used 150 g t^{-1} kerosene plus MIBC reagent was more successful in terms of separation than the other tests (Table 6). The main result of flotation was the successful transformation of the pyrophyllite samples into an end product consisting almost exclusively of pyrophyllite and kaolinite.

The chemical compositions of the NP and FC samples are listed in Table 7. The Al_2O_3 content (22.89%) in the NP sample increased in the concentrated products (26.50–30.32%; Table 7) due to increasing pyrophyllite and kaolinite contents. There was no significant difference in the SiO_2 contents between the NP and FC samples. The FC-1 concentrate with the smallest quartz content also had the smallest SiO_2 content (Tables 6 & 7). The LOI content decreased in FC-1 and FC-2 and increased in FC-3 and FC-4 compared to the NP sample. This result indicates that the FC-1 and FC-2 concentrates are enriched in pyrophyllite.

Discussion

Although various methods such as flotation, magnetic separation, gravity and leaching are used in pyrophyllite beneficiation,

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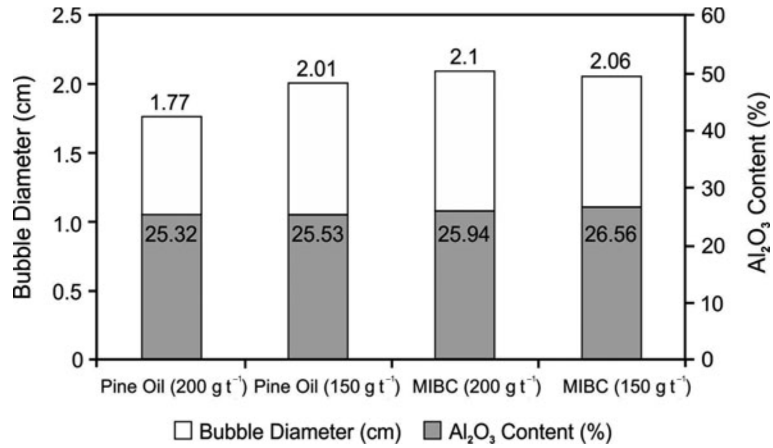

Fig. 7. Comparison of the effects of the single use of frothers on bubble diameter.

Table 4. Mixture effects of frothers with kerosene.

Dosages (g t^{-1})	Product	Weight (%)	SiO_2 (%) Cont.	SiO_2 (%) Distr.	Al_2O_3 (%) Cont.	Al_2O_3 (%) Distr.	LOI (%) Cont.	LOI (%) Distr.
75 + 75	Concentrate	37.34	64.14	34.22	27.17	45.98	5.21	41.95
Kerosene + MIBC	Tailings	62.66	73.48	65.78	19.02	54.02	4.30	58.05
	Total	100.00	69.99	100.00	22.06	100.00	4.64	100.00
75 + 75	Concentrate	38.54	67.08	36.80	24.08	42.63	5.70	45.62
Kerosene + pine oil	Tailings	61.46	72.26	63.20	20.33	57.37	4.26	54.38
	Total	100.00	70.26	100.00	21.78	100.00	4.81	100.00
400 + 150	Concentrate	57.78	65.70	54.75	26.63	65.91	5.40	68.12
Kerosene + pine oil	Tailings	42.09	74.31	45.25	18.85	34.09	3.46	31.80
	Total	100.00	69.24	100.00	23.32	100.00	4.58	100.00

Cont. = content, Distr. = distribution.

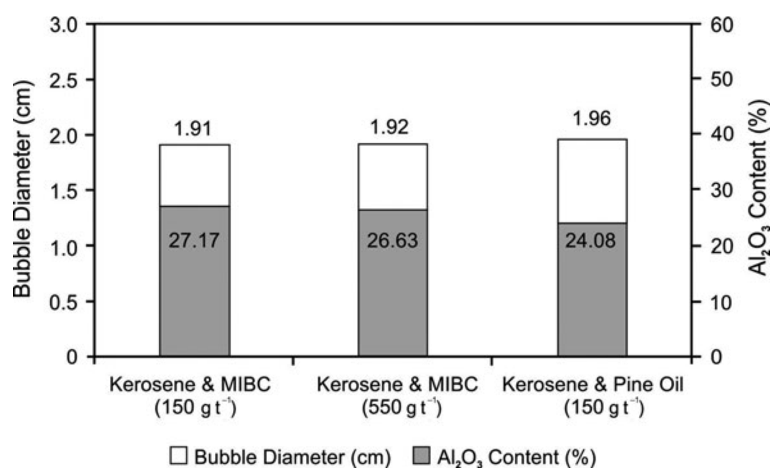

Fig. 8. Comparison of the effects of mixtures of frothers with kerosene on bubble diameter.

flotation is the most commonly used method, mainly because layered silicate minerals can float with any type of collector, even just a frother. The separation of pyrophyllite from other gangue minerals by froth flotation is made easier because pyrophyllite is naturally hydrophobic, easy-sliming and transports easily into flotation concentrates (Zhao *et al.*, 2019a).

In this study, flotation tests were carried out on Pütürge pyrophyllite ore and successful separation results with slight differences were obtained using various reagents and their combinations. Improved results were obtained when oil collectors were used together with the frothers. In the flotation rougher circuit, the most successful results were obtained for concentrates with 150 g t^{-1} kerosene plus pine oil and 150 g t^{-1} kerosene plus MIBC. Rougher concentrates contained 66.69 wt.% SiO_2 and 28.06 wt.% Al_2O_3 contents for kerosene plus MIBC and 64.26 wt.% SiO_2 and 29.76 wt.% Al_2O_3 for kerosene plus pine oil. In addition, kerosene plus frother mixtures were effective for the separation of the concentrates obtained from the cleaning circuits.

To enhance bubble particle aggregates, oily collectors such as kerosene and diesel are often used at small dosages to increase the surface hydrophobicity of naturally hydrophobic minerals such as molybdenite, talc and coal (Cao *et al.*, 2020).

Table 5. Cleaning effects in the flotation experiments.

Dosage (g t^{-1})	Product	Weight (%)	SiO_2 (%)		Al_2O_3 (%)		LOI (%)	
			Cont.	Distr.	Con.	Distr.	Cont.	Distr.
150	Concentrate (FC-1)	14.5	64.26	12.92	29.76	19.4	3.20	9.97
Kerosene + MIBC	Middling 2	7.5	63.53	6.81	27.30	9.2	7.02	11.34
	Middling 1	15.4	65.96	14.49	25.38	17.4	6.23	20.63
	Tailings	62.6	73.48	65.78	19.02	54.0	4.30	58.05
	Total	100.0	70.23	100.00	22.21	100.0	4.64	100.00
550	Concentrate (FC-5)	22.4	63.77	20.6	29.30	28.1	5.45	26.64
Kerosene + MIBC	Middling 2	7.4	65.59	7.0	25.63	8.1	5.83	9.34
	Middling 1	28.0	67.47	27.2	24.75	29.7	5.25	32.14
	Tailings	42.2	74.31	45.2	18.85	35.1	3.46	31.88
	Total	100.0	69.38	100.00	23.34	100.0	4.58	100.00
150	Concentrate (FC-3)	12.8	64.27	11.8	28.87	16.7	5.45	15.23
Pine oil	Middling 2	14.2	62.80	12.8	25.96	16.7	5.96	18.53
	Middling 1	17.4	65.26	16.4	22.63	17.8	5.62	21.36
	Tailings	55.6	73.79	59.0	19.40	48.8	3.70	44.88
	Total	100.0	69.53	100.0	22.10	100.0	4.58	100.00
150	Concentrate (FC-2)	10.7	66.69	10.2	28.06	13.9	4.00	8.91
Kerosene + pine oil	Middling 2	10.0	66.86	9.6	24.61	11.4	6.74	14.14
	Middling 1	17.7	66.64	16.8	22.35	18.3	6.13	22.57
	Tailings	61.4	72.26	63.4	19.85	56.4	4.26	54.38
	Total	100.0	69.98	100.0	21.60	100.0	4.81	100.00
200	Concentrate (FC-4)	10.3	66.29	10.0	27.26	12.3	5.45	10.18
Pine oil	Middling 2	12.0	64.01	11.2	25.70	13.5	6.73	14.74
	Middling 1	28.5	65.86	27.3	24.60	30.5	6.39	33.05
	Tailings	49.2	71.91	51.5	20.32	43.7	4..0	42.03
	Total	100.0	68.65	100.0	22.90	100.0	5.50	100.00

Cont. = content, Distr. = distribution.

However, the adsorption efficiency of oily collectors on mineral surfaces is relatively low as oily collectors are usually water-insoluble and show poor dispersion in aqueous solution. Previous work has demonstrated the role of surfactants in dispersing oily collectors in aqueous solution, which can be used to improve flotation recovery (Moxon *et al.*, 1988, Zhou *et al.*, 2017, Cao *et al.*, 2020). On the other hand, kerosene-type reagents spread on the solid surface as a thin layer, facilitating the adhesion of the solid to the bubble. The mixture of such reagents with frothers improves the flotation of naturally floating minerals (Bulatovic, 2007; Atak, 2017). In addition, variation in the bubble diameter was observed in both the rougher and cleaning circuits in the flotation experiments on Pütürge pyrophyllite ore. Although no obvious differences were observed, the bubble diameter increased slightly in the cleaning circuit. More research is needed to obtain more definitive results in this area.

The results of this study are compatible with previous flotation studies conducted on Pütürge pyrophyllite (Erdemoğlu & Sarıkaya, 1999; Erdem & Karaoğlu, 2005). In these studies, various frothers were examined in various amounts (50–200 g t^{-1}). The most successful results (61.5 wt.% SiO_2, 29.5 wt.% Al_2O_3 and 6.5 wt.% LOI) were obtained with 100 g t^{-1} MIBC (38–100 μm particle size, natural pH and 7–8 min flotation time; Erdem & Karaoğlu, 2005). Successful results have also been obtained in flotation studies using various collectors. Beneficiation using the flotation technique with dodecylamine as a collector reduced the quartz and coloured mineral contents and increased the brightness of the product (Das & Mohanty, 2009). Seo *et al.* (2020) investigated the efficiency of pyrophyllite

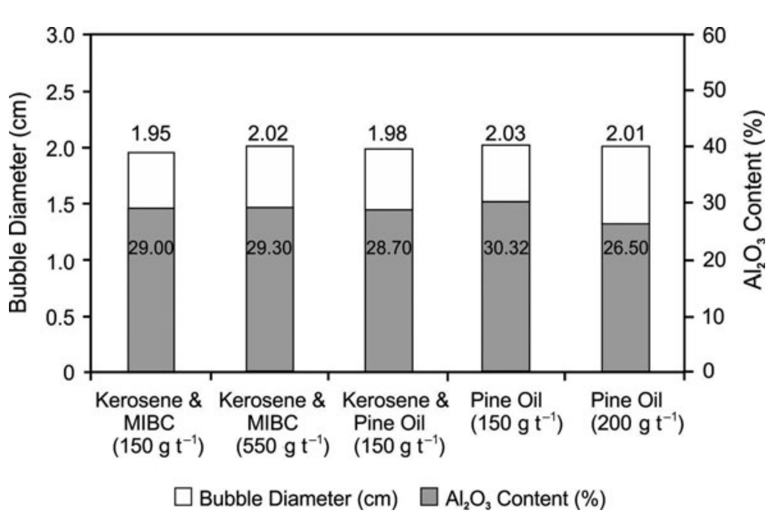

Fig. 9. Comparison of the effects of the cleaning circuits on bubble diameter.

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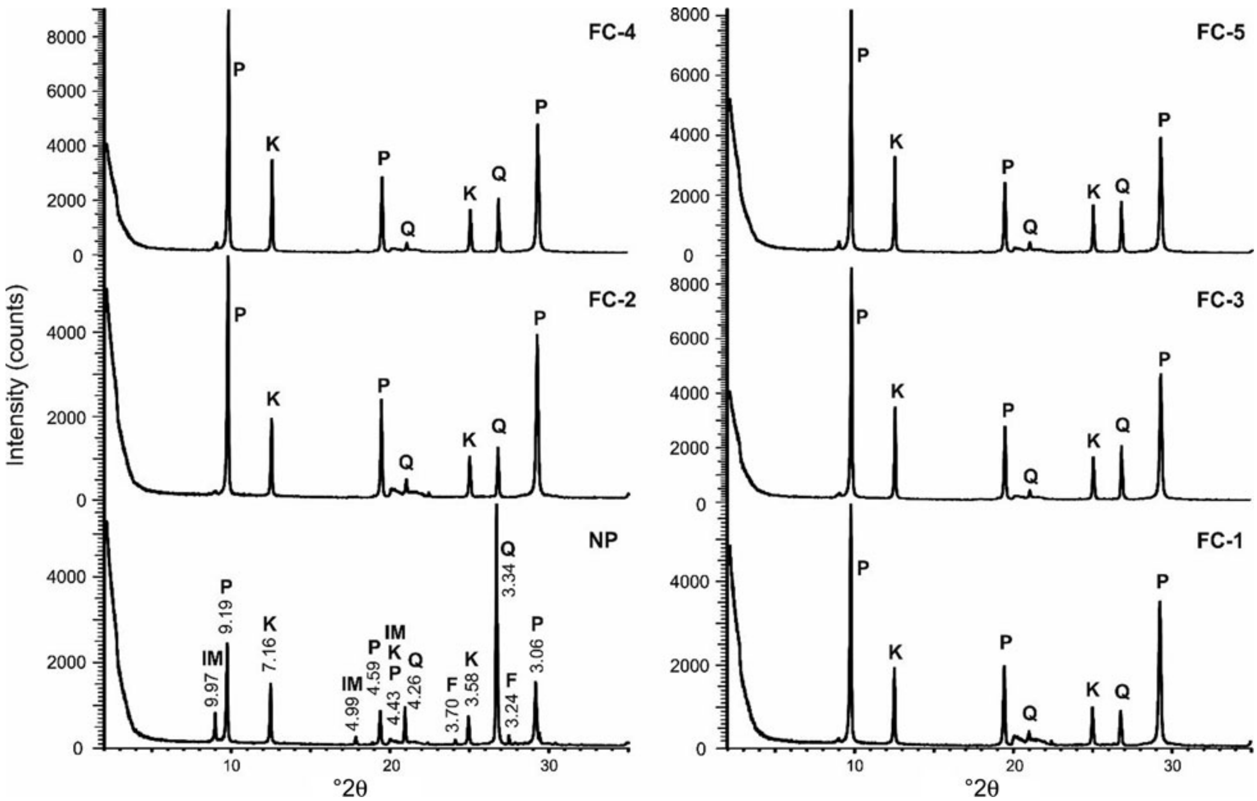

Fig. 10. Comparison of the greatest-intensity peaks for minerals on the XRD traces of the Pütürge pyrophyllite samples. Final concentrates: FC-1: with 150 g t^{-1} kerosene plus MIBC; FC-2: with 150 g t^{-1} kerosene plus pine oil; FC-3: with 150 g t^{-1} pine oil; FC-4: with 200 g t^{-1} pine oil; FC-5: with 550 g t^{-1} kerosene plus MIBC. F = feldspar IM = illite–mica, K = kaolinite, P = pyrophyllite, Q = quartz.

beneficiation using ammonium ions as the activator in the presence of an anionic collector, and they reported that the floatability of pyrophyllite increased with increasing anionic collector concentration at a low sodium oleate concentration. The effect of cationic collectors in flotation separation of diaspores from kaolinite, pyrophyllite and illite has been investigated using flotation tests (Zhong *et al.*, 2008). The flotation results for artificially mixed minerals showed that >65% kaolinite, pyrophyllite and illite were recovered and >80% of the diaspore was depressed. To investigate a novel class of effective silicate mineral collectors, the Gemini quaternary ammonium salt surfactant and its corresponding conventional monomeric surfactant (dodecyl trimethyl ammonium bromide; DTAB) were used to compare the flotation behaviours of illite, pyrophyllite and kaolinite (Xia *et al.*, 2009). The three silicate minerals with the Gemini surfactant as a collector demonstrated far greater floatability than with corresponding traditional collectors (Xia *et al.*, 2009). These studies show that ionic collectors are effective at separating pyrophyllite from quartz, which is a gangue mineral. However, the selectivity decreases when the gangue minerals are clay minerals such as illite and kaolinite.

In contrast to previous studies on pyrophyllite beneficiation, this work used a raw material containing a relatively large amount of pyrophyllite. Previous flotation studies on Pütürge pyrophyllite have not provided data on mineral ratios. However, based on their Al_2O_3 contents, the pyrophyllite samples in these previous studies contained less pyrophyllite than the sample used in this study. Another difference is that this study was carried out on a much finer-grained material. Thus, flotation is also successful for very-fine-grained materials. Obtaining more successful results with MIBC and pine oil in pyrophyllite flotation is also related to the fine particle size of the pyrophyllite. As the optimum size determined for pyrophyllite flotation is finer than 0.1 mm, it follows that alcohol-type frothers would be more efficient in such experiments. Dowfroth 250 is a glycol-type frother and is often effective in the flotation of coarse ores, while MIBC and pine

Table 6. Mineral percentages (wt.%) of the NP and FC pyrophyllite samples.

Sample	Pyrophyllite	Kaolinite	Quartz	Illite–mica	Feldspar
NP	40–45	20–25	20–25	10–15	<5
FC-1 (150 g t^{-1} kerosene + MIBC)	70–75	20–25	<5	Trace	–
FC-2 (150 g t^{-1} kerosene + pine oil)	75–80	15–20	5–10	Trace	–
FC-3 (150 g t^{-1} pine oil)	65–70	25–30	5–10	Trace	–
FC-4 (200 g t^{-1} pine oil)	65–70	25–30	5–10	Trace	–
FC-5 (550 g t^{-1} kerosene + MIBC)	60–65	25–30	5–10	Trace	–

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Table 7. Chemical composition (wt.%) of the NP and FC pyrophyllite samples.

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	LOI
NP	69.75	23.04	0.23	0.32	0.12	0.74	0.18	1.02	4.60
FC-1 (150 g t^{-1} kerosene + MIBC)	64.26	29.76	0.20	0.15	0.09	0.52	0.17	0.69	4.07
FC-2 (150 g t^{-1} kerosene + pine oil)	66.69	28.06	0.22	0.12	0.04	0.30	0.08	0.58	3.91
FC-3 (150 g t^{-1} pine oil)	64.27	28.87	0.20	0.22	0.06	0.39	0.17	0.71	5.11
FC-4 (200 g t^{-1} pine oil)	66.29	27.26	0.20	0.19	0.05	0.31	0.10	0.54	5.06
FC-5 (550 g t^{-1} kerosene + MIBC)	63.77	29.30	0.18	0.20	0.08	0.43	0.11	0.65	5.65

oil are alcohol-type frothers that are effective in the flotation of fine-sized ores (Khoshdast & Sam, 2011; Ngoroma *et al.*, 2013).

Increasing the efficiency of pyrophyllite flotation is generally associated with increasing Al_2O_3 content. However, if kaolinite is present in addition to pyrophyllite, it is useful to check the mineralogical compositions of the beneficiation products. As the Pütürge pyrophyllite material used in this study contains 40–45% pyrophyllite and 20–25% kaolinite, the flotation results were checked mineralogically along with the chemical compositions. A significant trend holds between the Al_2O_3 contents of the studied samples and the pyrophyllite and kaolinite peak intensities on the XRD traces. The relative peak intensities of pyrophyllite and kaolinite were also comparable. The XRD RIRs of these two minerals can be considered similar, as they have similar chemical compositions, similar morphologies, their crystal systems are triclinic (space group P1) and their crystallographic parameters are comparable (a:b:c = 0.5761:1.0000:1.0439 or a = 5.160 Å, b = 8.993 Å, c = 9.360 Å for pyrophyllite and a:b:c = 0.5755:1.000:0.8253 for kaolinite; Wardle & Brindley, 1972; Bish & Von Dreele, 1989; Bentayeb *et al.*, 2003). On the other hand, the presence of kaolinite in pyrophyllite ores may be beneficial in terms of some usages of these ores. The flexural strength increases with the addition of kaolinite, especially in the production of ceramic composites (Jeong *et al.*, 2017). Therefore, pyrophyllite and kaolinite should be considered as useful minerals, and the remaining minerals should be considered as gangue minerals. Therefore, the total pyrophyllite plus kaolinite content (65%) in Pütürge ore increased to 90–95% after flotation, whereas gangue-mineral contents (quartz, feldspar and illite–mica) decreased from 35–40 wt.% to <10 wt.%.

Conclusions

The Pütürge pyrophyllite is currently used mainly in white-cement production. The NP sample contains moderate amounts of pyrophyllite (40–45 wt.%), kaolinite (20–25 wt.%) and quartz (20–25 wt.%) and minor amounts of illite–mica (10–15 wt.%) and feldspar (<5 wt.%). After beneficiation with flotation, pyrophyllite was enriched in the concentrated products. The pyrophyllite content in all FC samples was 60–80 wt.%. There was no significant change in kaolinite abundance. On the other hand, quartz, illite–mica and feldspar either decreased or disappeared. The total amount of pyrophyllite and kaolinite increased from ~65 wt.% in the NP sample to 90–95 wt.% in the concentrated products. The main factors controlling the Al_2O_3 content in the samples were pyrophyllite and kaolinite abundance. The SiO_2 content was affected by of both these minerals and by the quartz percentage.

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