Enrichment of wollastonite with high calcite content

Ceyda Şavran, Tülay Türk, Ganjinakhon Irgasheva, Murat Olgaç Kangal

Istanbul Technical University, Faculty of Mines, Mineral Processing Engineering Department, 34469, Maslak, Istanbul, Turkey

Corresponding author: savranc15@itu.edu.tr (Ceyda Şavran)

Abstract: Wollastonite plays a significant role as an industrial raw material in many fields; its exclusive properties mean that it is used in ceramics, paint, metallurgy and coatings. In nature, wollastonite mostly occurs with calcite. While the most common method for separating wollastonite from calcite is calcination, flotation is one of the methods for separating two minerals in a more economic, environmentally friendly way. In this study, the ore contains a large amount of calcite and augite, which is an iron bearing mineral that is subjected to magnetic separation, followed by flotation in order to obtain wollastonite and calcite concentrations individually. The SiO_2, CaO and Fe_2O_3 contents in the ore are 28.00%, 48.20% and 0.45%, respectively. After magnetic separation has reduced the iron content, flotation experiments are carried out to find the optimum conditions. For the flotation process, the effect of particle size, pH and collector dosage are investigated. A wollastonite concentration of 84% purity is successfully achieved, with a 0.17% iron concentration under the optimal conditions of 100 micron particle size, pH 8 and 500 g/t collector dosage. The purity of the calcite is raised to 95% with the application of a cleaning stage.

Keywords: wollastonite, calcite, flotation, magnetic separation, lankropol OPA

1. Introduction

Wollastonite is an industrial raw material consisting of calcium metasilicate. It forms as a product of thermal metamorphism at the contact of igneous rocks and limestones (Haner and Çuhadaroğlu, 2013). The formation reaction of wollastonite is given in Eq. (1).

$$SiO_2 + CaCO_3 = CaSiO_3 + CO_2 \qquad (1)$$

Wollastonite is rarely encountered in its purest form in nature but is associated with a variety of gangue minerals, such as garnet, calcite, epidote, quartz, diopside, and augite. Wollastonite production is restricted around the world, due to its complex structure (Bulatovic, 2005). Calcite (calcium carbonate ($CaCO_3$)) is the most abundant mineral in the earth's crust and coexists with apatite, scheelite, and fluorite. The most effective way to extract calcite from other calcium-containing minerals is through flotation. Nevertheless, the selective flotation of calcite is challenging, while other minerals have Ca ions in their structure (Gao et al., 2017).

Wollastonite's unique cleavage qualities give it an acicular or plate-like form after crushing and grinding. Its high-strength mineral properties have a wide range of applications in a variety of industries. Despite its needle-like form, wollastonite has begun to be employed to replace other fibrous raw materials because it has no negative health effects (Haner and Çuhadaroğlu, 2013). In addition to the ceramics industry, which covers the widest part of its usage area, it is widely used in the production of paint, plastic, rubber, metallurgy, glass, welding electrode production, and Portland Cement, as a filling material (Çinku et al., 1997).

Because of high level of purity, whiteness, and affordability of calcite, its fine particles are used in numerous industries. It is used in the paper, paint, plastic, medicine, agriculture, glass, cosmetics and a variety of other industries, including the construction industry, which is the largest usage area (DPT,

2001). The necessary requirements for wollastonite and calcite to be able to be used in each industry are given in Tables 1 and 2, respectively.

Table 1. Mineralogical properties of wollastonite according to usage area (MTA, nd)

Usage Area	Purity	Specifications
Paint making	Min. 90% wollastonite	Over 90% brightness
Plastic and Filling Quality	Min. 95% wollastonite	Min. 90% brightness
Ceramic and Glaze Quality	Min. 95% wollastonite	Min. 90% brightness
Ceramic Quality	Min. 90% wollastonite	Max. 4% loss of fire, Max. 0.3% Fe_2O_3
Metallurgical Quality	Min. 80% wollastonite	1% Al_2O_3 content and 0.02 S/P ratio
Mineral Wool Quality		Min. 20:1 aspect ratio

Table 2. Mineralogical properties of calcite according to usage area (Şahin, 2008)

Usage Area	Purity	Size	Specifications
Paper		1-100 μ	Min. 94% brightness
Paint	95% $CaCO_3$		
Rubber	Min. 92% $CaCO_3$	Less than 20 μ	
Plastic	Min. 95% $CaCO_3$	0.02-3 μ	High brightness
Animal feed	Min. 92% $CaCO_3$	25 μ (All large animals) 400 μ (Chick) 3 mm (Barnyard fowl)	Max. 3% impurities
Agriculture	Min. 90% $CaCO_3$	Less than 150 μ	Max. 4 ppm As
Pharmacy	98.8% $CaCO_3$	Less than 2.4 μ	Max. 0.05%
Coal mine		Less than 84 μ	Max. 4% SiO_2 Max. 5% flammable material
Glass	98.5% $CaCO_3$	Less than 500 μ	0.2% Fe
Glass cement	90% $CaCO_3$	Less than 40 μ	
Sugar	96% $CaCO_3$	Less than 74 μ	0.5% SiO_2
Cosmetic	98% $CaCO_3$	Less than 0.4 μ	38-88% brightness
Explosive	98% $CaCO_3$	Larger than 125 μ	
Water treatment	90% CaO (for hardness) 93% CaO (for color)		Max. 0.3% Fe_2O_3
Ceramic	Min. 98% $CaCO_3$		
Joint material	Min. 95% $CaCO_3$	Less than 250 μ	Max. 1% moisture (for white cement)

Although the required purity levels vary by sector, the appropriate purity for the usage of wollastonite is often greater than 90%, as shown in Table 1. In fact, it is preferable that these percentages approach 97%. The iron content of wollastonite must be retained in precise proportions and separated from calcite, in order to be utilized as a raw material in glass, ceramic, plastic, or filler. Despite the fact that the beneficiation processes used in this case vary, depending on the ore deposit, specific enrichment procedures were chosen for wollastonite.

A calcite content of at least 90% is generally preferred for use in industry, as shown in Table 2. Size, brightness, and impurities (such as SiO_2, Fe, and As content) are essential characteristics that differ by industry.

Despite the fact that sorting and magnetic separation are the most widely employed mineral processing methods, flotation applications have also been tested in several studies. However, because the gangue minerals in wollastonite have similar floatability properties, flotation, as an enrichment process, is complicated and difficult to implement. Some physical enrichment methods, such as magnetic separation, are generally utilized. Several studies have been carried out in which magnetic separation is applied, either before or after flotation in the systems (Ravi et al., 2014; Marchevskaya et al., 2017). The ideal method for flotation applications is reverse flotation or bulk flotation because the

minerals found nearby have a higher floatability than wollastonite. If calcite and other gangue minerals are present, the calcite mineral is expected to float first, followed by the gangue minerals, and then the wollastonite. Calcite is floated using sulfate salts, while gangue minerals are floated with amines (Bulatovic, 2005).

The primary goal of this work is to produce wollastonite and calcite with the necessary specifications. Magnetic separation is applied to achieve low iron content for both wollastonite and calcite. Flotation is carried out to separate wollastonite and calcite after magnetic separation. Lankropol OPA is employed as an anionic collector in the flotation tests but is not described in the literature for this type of ore. Although calcination is the most widely used method of separating calcite from wollastonite, flotation can be more cost-effective and environmentally beneficial.

2. Materials and methods

2.1. Materials

Wollastonite ore with high calcite content was obtained from the Buzlukdağı Region, Kırşehir, Turkey. The representative sample was crushed by jaw, cone, and roll crushers (Ersel Heavy Machine, Turkey) until its particles below 2 mm. Sieving was then carried out, in order to determine the particle size distribution; the d_{80} size of the ore was found to be 1.2 mm. The BSE (Back-Scattered Electron) image of the samples is given in Fig. 1. The chemical content of the ore (Table 3) was determined by inductively coupled plasma (ICP) at the Activation Laboratories Ltd., Canada.

X-ray diffraction (XRD) analysis was conducted with a copper X-ray-sourced Panalytical X'Pert Pro diffractometer (Malvern Panalytical Ltd, Malvern, UK). PDF4/Minerals ICDD software was used for mineral characterization. The crystals' mineral phase ratios were determined by the Rietveld method. The XRD pattern of wollastonite ore is shown in Fig. 2. According to the XRD results, the ore contains mostly wollastonite and calcite minerals.
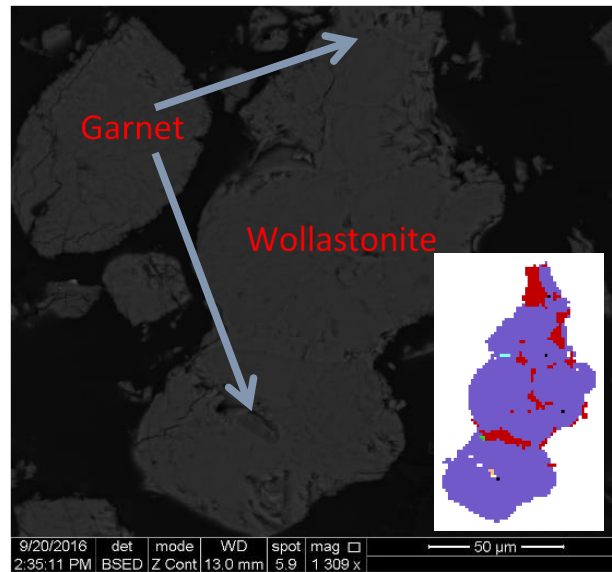

Fig. 1. BSE image of wollastonite ore

Table 3. Chemical analyses of a representative sample of wollastonite ore

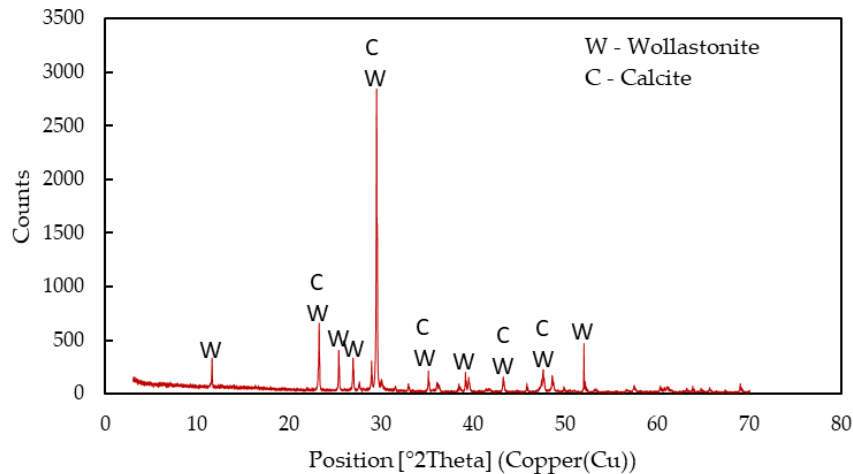| Compound	Content, %	Compound	Content, %
SiO_2	28.00	CaO	48.20
Al_2O_3	1.91	MgO	1.15
Fe_2O_3	0.45	P_2O_5	0.03
TiO_2	0.04	SrO	0.04
Na_2O	0.47	MnO	0.03
K_2O	0.40	LOI	20.80

LOI: Loss on Ignition

Fig. 2. X-ray diffraction patterns of wollastonite ore

According to the Table 3, the purities of wollastonite and calcite is calculated as 46.7% and 47.3%, respectively. The chemical and mineralogical properties of the samples were defined with differential thermal analysis (DTA) and thermogravimetric analysis (TGA) equipment (using a STA 449 F3 Jupiter® thermal analyzer, NETZSCH, Selb, Germany). The DTA and TGA curves of wollastonite ore are given in Fig. 3. As can be seen there, as the temperature increases from 700 to 950°C, the wollastonite ore loses 21% of its weight. Calcite, which makes up around 50% of the ore's structure according to the chemical analyses (Table 3), is the primary cause of this loss. Mineral liberalization analysis was performed with a FEI MLA 650F analyzer (Hillsboro, OR, USA). According to the liberation analysis, shown in Fig. 4, wollastonite and calcite are liberated below 200 μm and 150 μm, with a liberation degree of about 96% and 95%, respectively.
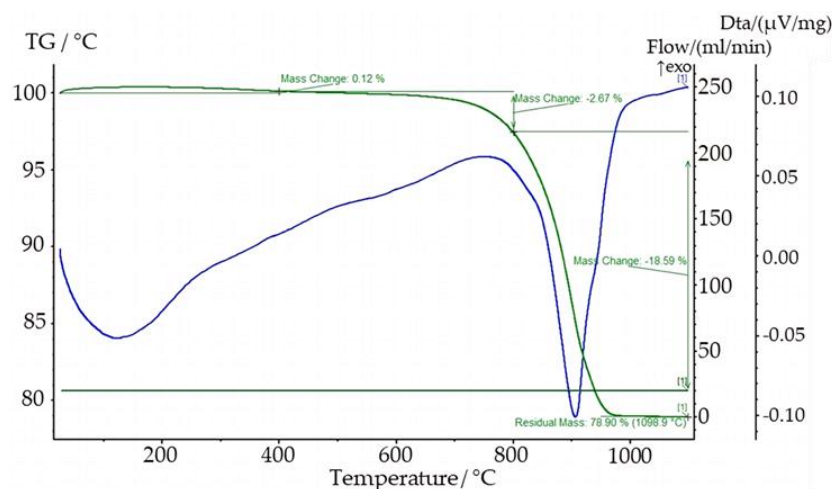

Fig. 3. DTA-TGA curves of wollastonite ore

2.2. Experimental procedures

In the first part of the study, the surface characteristics of the wollastonite and calcite samples were determined with zeta potential measurements. After concluding the surface characteristics of the samples, the ore was separated into four size groups (+2 mm, -2+1 mm, -1+0.5 mm, and -0.5 mm) to discriminate the iron (augite) from the ore. Flotation experiments were then carried out for different particle sizes, pH values, and collector dosages, with the obtained nonmagnetic product. All tests and chemical analyses were repeated three times, to ensure accuracy. As a result, it was determined that the error estimation for chemical analysis was roughly ±1% for each result. Consequently, the arithmetical mean of three extraction values from the analysis was determined, and the potential error factor was then assessed.
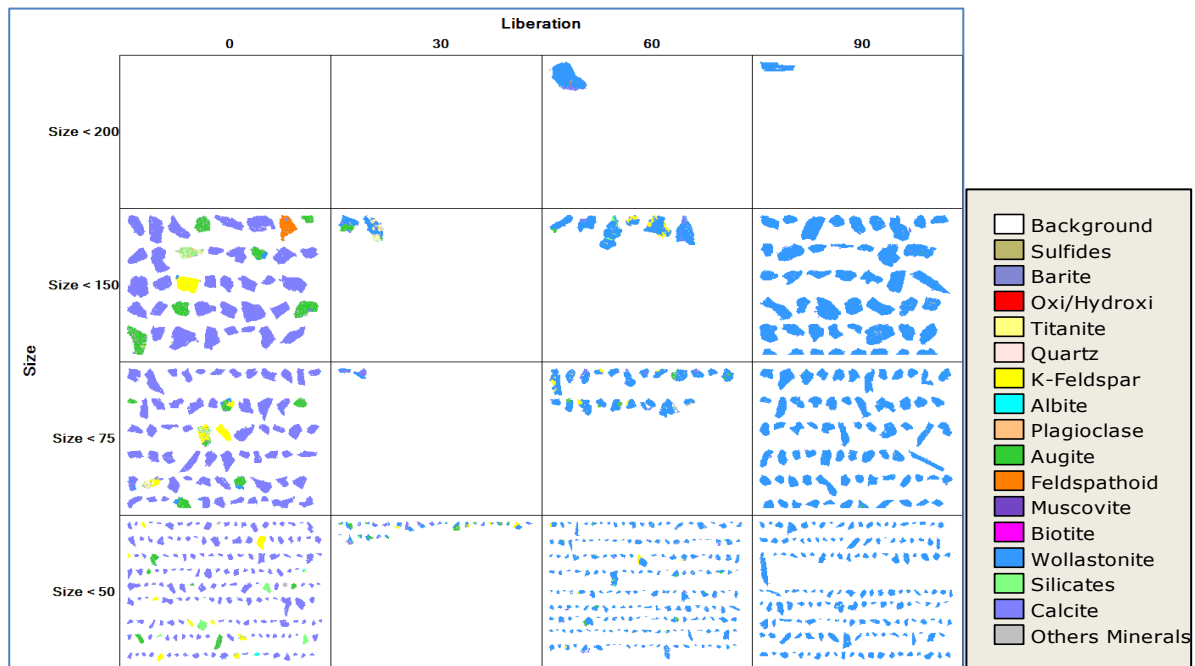
Fig. 4. Mineral liberation analysis of the sample

2.2.1.   Zeta potential measurements

The zeta potential values of particles provide their surface characteristics in a definite medium and show their affinity. The surface characteristics of wollastonite and calcite were determined using a microprocessor-equipped Zeta-Meter 3.0+ model instrument. In the zeta potential measurements, pure wollastonite and calcite samples were used to determine surface charge. All experiments were carried out under 75 V and the K factor was 0.71 cm^{-1}. Diluted hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH of the suspension and obtain the zeta potential of particles according to the changing pH values. The electricity was applied to the suspension, which contained 0.1 grams of sample and 100 ml of distilled water in a wide pH range. The zeta potential was measured, according to the voltage of electricity applied and the mobility of particles under the effect of the electricity.

2.2.2.   Magnetic separation experiments

In order to remove 0.45% Fe_2O_3 content from the raw ore, high density dry disc magnetic separation was used for +2 mm, -2+1 mm, and -1+0.5 mm size groups. Since the -0.5 mm size group is not suitable for REMS (Rare Earth Magnetic Separator), no testing was performed. The disc speed was kept constant at 80 RPM and the blade angle was adjusted according to the obtained product over the magnetic separation process. After, the obtained nonmagnetic product and -0.5 mm size group were blended and proceeded to flotation experiments.

2.2.3.   Flotation experiments

The nonmagnetic product obtained from REMS was combined with the -0.5 mm size group and all samples were ground in a laboratory-type ceramic mill (Refsan, Turkey) with a 60% solid ratio and 40% ball charge. Samples were ground for 15, 8, and 5 minutes, to obtain 100, 200, and 300 micron particles, respectively. The reverse flotation method was then applied, to selectively separate wollastonite, calcite, and iron-bearing minerals, with the addition of Lankropol OPA (an alkyl sulphonate) as a collector. Different particle sizes (100, 200 and 300 microns), pH (6, 6.5, 7, 7.5, 8, 8.5, 9) and collector dosages (250, 500, 1000 g/t) were investigated to determine the optimal enrichment conditions. Flotation tests were carried out in a Denver cell with a 20% solid ratio. A 1.5 L volume cell was used at 1300 rpm flotation speed, 5 minutes of conditioning and 2 minutes of flotation. In the trials, calcite was floated in the first three stages, whereas augite was predominant in the fourth stage, and the sinking product is obtained

as a wollastonite concentrate. After the rougher flotation, the floated products from the first three stages were mixed and applied to the cleaning flotation.

3.   Results and discussion

3.1.   Results of zeta potential measurements

The zeta potential measurements were performed for varied pH values, for both wollastonite and calcite samples. The results of the measurements are given in Fig. 5 and Fig. 6 for pure wollastonite and pure calcite samples, respectively.
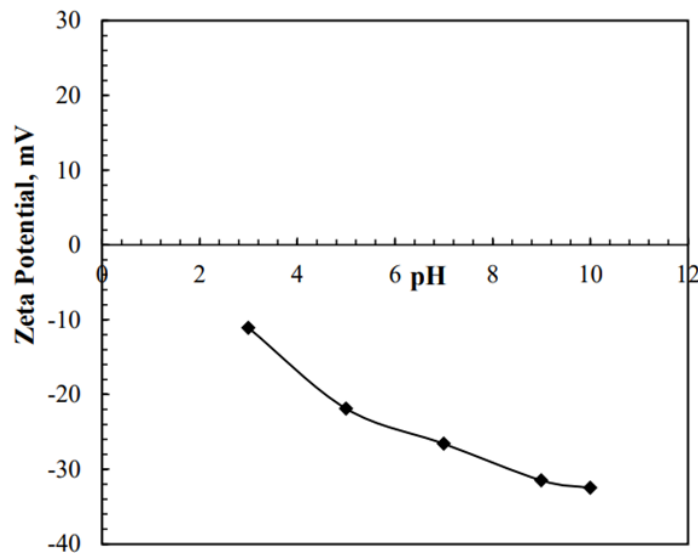
Fig. 5. The zeta potential profile of wollastonite vs. pH values
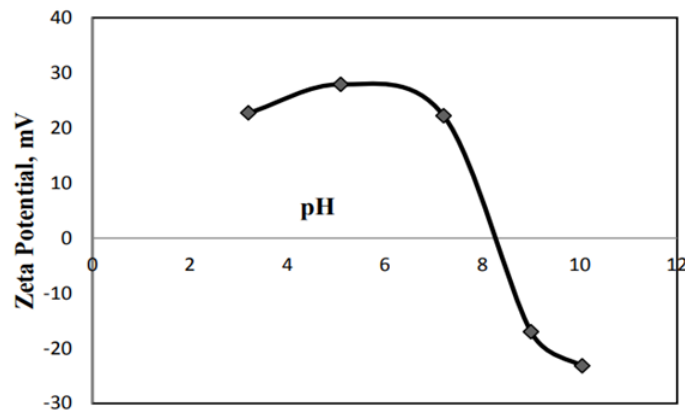
Fig. 6. The zeta potential profile of calcite vs. pH values

According to the results of the zeta potential experiments (Fig. 5), wollastonite shows a negative trend with increasing pH values. Since the wollastonite surface is negative at low pH values, it became more negative upon increasing OH$^-$ content, which is in accordance with the literature (Oelkers et al., 2009; Chen et al., 2020). On the contrary, calcite shows relatively acidic pH values, while the zeta potential values were measured in the range +20 to +30 mV, suddenly decreasing to -20 over a pH value of 8.5. In the literature, zeta potential measurements were carried out at a pH range of 6 to 12 because of the basic characteristics of calcite (Al Mahrouqi et al., 2017). However, a few studies which also studied acidic conditions (Chen et al., 2020), showed similar results to Fig. 6.

The measurements of both wollastonite and calcite samples demonstrated that wollastonite and calcite separation can be achieved in the pH range 2-8, by using anionic-type collectors, such as sulphonate collectors.

3.2. Results of magnetic separation experiments

Magnetic separation experiments are carried out as a pre-enrichment process. With the magnetic separation, Fe_2O_3 contents for all particle sizes, decreased in the nonmagnetic product. Table 4 shows that, for the particle sizes of +2, -2+1, and -1+0.5 mm, magnetic products contain Fe_2O_3 with distributions of 30%, 20%, and 25%, respectively. The results of magnetic separation by size groups are given in Table 4.

Table 4. Results of magnetic separation experiments

Particle size (mm)	Product	Weight (%)	Fe_2O_3		CaO		SiO_2		Loss of ignition
			C	D	C	D	C	D	
+2	Magnetic	18.0	1.02	29.2	41.20	17.0	38.90	19.4	11.23
	Nonmagnetic	82.0	0.55	71.6	44.40	83.1	35.50	80.6	14.95
	Total	**100.0**	**0.63**	**100.0**	**43.82**	**100.0**	**36.10**	**100.0**	**14.28**
-2 + 1	Magnetic	8.3	3.00	20.0	32.20	6.5	43.40	10.2	7.63
	Nonmagnetic	91.7	1.10	80.7	42.20	93.5	34.80	89.9	14.10
	Total	**100.0**	**1.25**	**100.0**	**41.36**	**100.0**	**35.50**	**100.0**	**13.56**
-1 + 0.5	Magnetic -1	11.4	4.01	15.8	30.60	8.6	44.00	15.7	7.43
	Magnetic -2	10.2	2.87	10.1	34.20	8.6	34.20	11.0	25.26
	Middling	39.2	1.58	21.4	38.20	36.9	37.20	45.8	13.78
	Nonmagnetic	39.2	0.39	5.3	47.70	46.0	22.40	27.6	9.44
	Total	**100.0**	**2.89**	**100.0**	**40.65**	**100.0**	**31.82**	**100.0**	**12.53**
-0.5	Total	100.0	0.48	100.0	47.90	100.0	27.30	100.0	21.00
	TOTAL		**1.67**		**42.58**		**32.84**		

C: Content, D: Distribution

According to the magnetic separation results shown in Table 4, iron is mostly in the -1+0.5 mm size group. Since the liberation of the minerals are not enough in the coarse size, there are losses of wollastonite and calcite content and some of the material goes to the magnetic product. Therefore, magnetic separation is most suitable in the -1+0.5 mm size group, for this sample.

3.3. Effective parameters in the flotation process

Flotation experiments were carried out on the nonmagnetic product obtained from the magnetic separation of the -0.5 mm size sample. The effects of particle size, pH, and collector dosage were investigated. After the determination of optimum conditions, wollastonite concentrations were obtained with low Fe_2O_3 contents and calcite was obtained with high purity. The purity levels are calculated by dividing by the respective molecular weights of each mineral and utilizing the loss on ignition for calcite and the SiO_2 contents for wollastonite.

3.3.1. Particle size

100, 200, and 300 microns particle sizes were chosen for the experiments. The sample was ground for 15, 8, and 5 minutes to obtain 100, 200, and 300 microns, respectively. The collector was added 500 g/t, and the experiment was performed at natural pH. The graphical result is given in Fig. 7 and the results of the experiments, depending on the particle size, are given in Table 5.

Despite the fact that the content of the sinking product was similar for each size-dependent experiment, when calcite and iron concentrations were also taken into account, the best result was obtained with 86.48% content and 70.8% recovery. In comparison to other particle sizes, the largest efficiency of wollastonite was obtained at 100 microns. Particle size was kept constant in the following experiments.
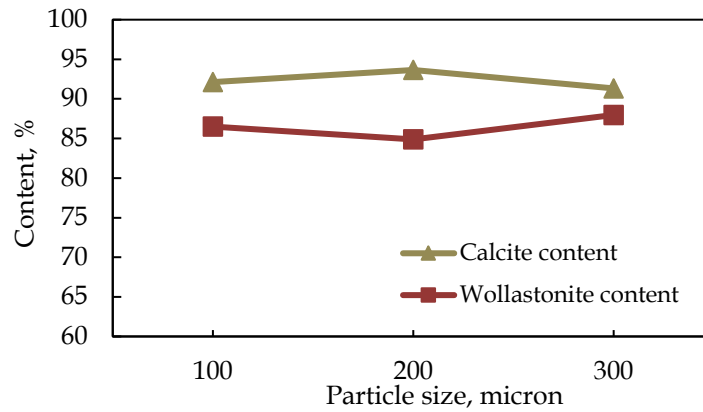
Fig. 7. Graphical demonstration of the particle size experiment

Table 5. Results of particle size experiments

Particle size, mm	Product	Weight %	Fe$_2$O$_3$		Loss of ignition		Calcite		Wollastonite	
			C	D	C	D	P	D	P	D
300 microns	Float-1	15.6	0.05	2.2	40.63	28.8	92.34	28.8	4.30	1.6
	Float-2	25.5	0.1	7.0	39.91	46.2	90.70	46.2	6.00	3.6
	Float-3	19.7	0.59	32.1	25.07	22.5	56.98	22.5	34.13	16.0
	Float-4	13.6	0.38	14.2	1.95	1.2	4.43	1.2	80.48	25.9
	Float-5	11.7	1.27	41.0	1.13	0.6	2.57	0.6	85.37	23.7
	Sink	14.0	0.09	3.5	1.11	0.7	2.52	0.7	87.97	29.2
	Total	**100.0**	**0.36**	**100.0**	**22.00**	**100.0**	**49.99**	**100.0**	**42.11**	**100.0**
200 microns	Float-1	16.7	0.05	5.1	41.59	31.8	94.52	31.8	3.05	1.2
	Float-2	27.1	0.11	18.4	40.97	50.9	93.11	50.9	5.52	3.5
	Float-3	11.0	0.64	43.5	28.43	14.4	64.61	14.4	25.70	6.7
	Float-4	7.0	0.01	0.4	2.86	0.9	6.50	0.9	75.98	12.6
	Float-5	9.8	0.25	15.1	1.87	0.8	4.25	0.8	84.12	19.5
	Sink	28.3	0.1	17.4	0.9	1.2	2.05	1.2	84.88	56.6
	Total	**100.0**	**0.16**	**100.0**	**21.82**	**100.0**	**49.59**	**100.0**	**42.49**	**100.0**
100 microns	Float-1	19.4	0.07	5.1	41.5	37.0	94.32	37.0	4.15	2.0
	Float-2	26.8	0.18	18.2	39.84	49.1	90.55	49.1	7.23	4.8
	Float-3	10.9	0.9	37.0	23.11	11.6	52.52	11.6	14.30	3.8
	Float-4	6.1	1.04	23.9	2.43	0.7	5.52	0.7	75.23	11.3
	Float-5	3.7	0.32	4.5	2.63	0.4	5.98	0.4	79.60	7.3
	Sink	33.1	0.09	11.2	0.79	1.2	1.80	1.2	86.48	70.8
	Total	**100.0**	**0.26**	**100.0**	**21.75**	**100.0**	**49.43**	**100.0**	**40.48**	**100.0**

C:Content, D:Distribution, P:Purity

3.3.2. pH

After a suitable particle size was obtained, the effect of pH was investigated at several values (6, 6.5, 7, 7.5, 8, 8.5, 9). The collector dosage was kept constant (500 g/t) and different pH values were adjusted with HCl. The graphical result is given in Fig. 8 and the results of the experiments depend on the pH values given in Table 6.

The results in Table 6 indicate that pH values had a considerable effect on the calcite and wollastonite purities and Fe$_2$O$_3$ contents. Wollastonite purities increased continuously with increasing pH. However, it decreased after pH 8. On the other hand, yields decreased after pH 7.5. However, calcite purities and Fe$_2$O$_3$ contents need to be evaluated because the calcite purity increased from pH 7.5 to 8 and Fe$_2$O$_3$

contents decreased at pH 8, for both wollastonite and calcite; pH 8 is selected as the optimum. As can be seen in Fig. 5 and 6, separation was performed using an anionic collector at pH 8. Moreover, Fig. 8 clearly shows that the wollastonite content stars to decrease at a pH value of 8, while calcite content stayed about the same.
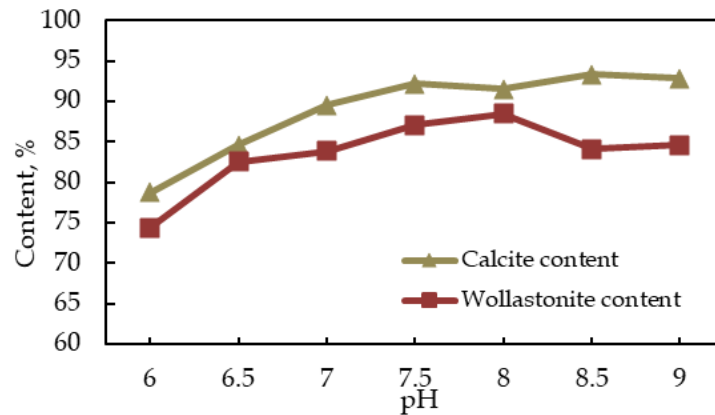

Fig. 8. Graphical demonstration of the pH values experiment

Table 6. Results of pH values experiments

pH	Product	Weight %	Fe$_2$O$_3$		Loss of ignition		Calcite		Wollastonite	
			C	D	C	D	P	D	P	D
6	Float-1	16.4	0.11	7.6	40.58	29.9	92.23	29.9	2.12	0.9
	Float-2	27.5	0.17	19.6	38.76	48.0	88.09	48.0	6.77	4.8
	Float-3	17.2	0.62	44.7	22.44	17.3	51.00	17.3	33.62	14.9
	Float-4	12.3	0.34	17.6	3.4	1.9	7.73	1.9	77.83	24.8
	Float-5	12.7	0.12	6.4	1.63	0.9	3.70	0.9	83.87	27.5
	Sink	14.0	0.07	4.1	2.98	1.9	6.77	1.9	74.40	27.1
	Total	**100.0**	**0.24**	**100.0**	**22.19**	**100.0**	**50.43**	**100.0**	**38.60**	**100.0**
6.5	Float-1	15.3	0.06	4.3	40.96	28.5	93.09	28.5	1.82	0.7
	Float-2	29.2	0.08	10.8	40.57	53.9	92.20	53.9	5.02	3.6
	Float-3	12.5	0.56	32.5	24.92	14.2	56.64	14.2	28.57	8.8
	Float-4	7.7	0.95	34.2	2.7	1.0	6.14	1.0	76.10	14.5
	Float-5	10.9	0.18	9.1	1.2	0.6	2.73	0.6	84.22	22.7
	Sink	24.4	0.08	9.1	1.69	1.9	3.84	1.9	82.53	49.7
	Total	**100.0**	**0.22**	**100.0**	**21.96**	**100.0**	**49.90**	**100.0**	**40.53**	**100.0**
7	Float-1	11.2	0.06	1.7	39.86	20.7	90.59	20.7	4.43	1.2
	Float-2	26.3	0.05	3.2	40.76	49.6	92.64	49.6	3.17	2.0
	Float-3	15.4	1.19	45.4	36.82	26.3	83.68	26.3	9.15	3.4
	Float-4	8.4	1.47	30.6	2.98	1.2	6.77	1.2	71.30	14.6
	Float-5	7.8	0.55	10.6	1.31	0.5	2.98	0.5	82.63	15.7
	Sink	30.9	0.11	8.4	1.15	1.6	2.61	1.6	83.85	63.0
	Total	**100.0**	**0.40**	**100.0**	**21.6**	**100.0**	**49.0**	**100.0**	**41.08**	**100.0**

3.3.3. Collector dosage

Flotation experiments were carried out to investigate the collector (Lankropol OPA) dosage at various values (250, 500, 1000 g/t). Particle size and pH were maintained at 100 microns and 8, respectively. The results are presented in Table 7 and the graphical result is given in Fig. 9.

As seen in Table 7, 250 g/t collector dosage is not considered sufficient because of the low calcite and wollastonite content, along with the separation efficiency. Even though calcite distribution is high

(with a 1000 g/t collector dosage), wollastonite distribution is quite low and the iron contents for second and third stage products are higher, compared with 500 g/t. Therefore, a 500 g/t collector dosage was preferred. In a different study carried out in the same area, potassium oleate was used in the flotation of calcite, and the optimum conditions were obtained at a size of 100 microns, a collector of 1500 g/t,

Table 6 (cont'd). Result of pH values experiments

|										
	Float-1	5.2	0.15	2.8	37.71	8.9	85.70	8.9	6.30	0.8
	Float-2	17.4	0.07	4.4	41.5	32.8	94.32	32.8	2.63	1.1
	Float-3	26.7	0.1	9.7	40.51	49.4	92.07	49.4	4.77	3.0
7.5	Float-4	8.6	0.96	29.9	16.63	6.5	37.80	6.5	46.30	9.4
	Float-5	7.2	1.12	29.2	1.41	0.5	3.20	0.5	78.33	13.4
	Sink	34.9	0.19	24.1	1.21	1.9	2.75	1.9	87.05	72.3
	Total	**100.0**	**0.28**	**100.0**	**21.95**	**100.0**	**49.89**	**100.0**	**42.07**	**100.0**
	Float-1	13.8	0.09	5.8	39.36	22.8	89.45	22.8	7.55	2.6
	Float-2	18.5	0.06	5.2	41.39	32.2	94.07	32.2	2.25	1.0
	Float-3	24.5	0.13	14.9	39.92	40.9	90.73	40.9	10.77	6.5
8	Float-4	7.3	1.25	42.9	5.64	1.7	12.82	1.7	67.93	12.3
	Float-5	6.7	0.29	9.1	1.57	0.4	3.57	0.4	82.53	13.7
	Sink	29.2	0.16	22.0	1.63	2.0	3.70	2.0	88.45	63.9
	Total	**100.0**	**0.21**	**100.0**	**23.86**	**100.0**	**54.24**	**100.0**	**40.40**	**100.0**
	Float-1	6.3	0.08	1.9	40.11	11.6	91.16	11.6	5.08	0.8
	Float-2	16.0	0.06	3.6	41.67	30.6	94.70	30.6	1.10	0.4
	Float-3	23.2	0.09	7.3	40.96	43.4	93.09	43.4	1.88	1.1
8.5	Float-4	10.7	0.84	32.7	24.43	11.9	55.52	11.9	31.67	8.4
	Float-5	13.1	0.77	36.6	1.58	0.9	3.59	0.9	78.78	25.5
	Sink	30.7	0.16	17.9	1.09	1.5	2.48	1.5	84.13	63.9
	Total	**100.0**	**0.27**	**100.0**	**21.87**	**100.0**	**49.70**	**100.0**	**40.44**	**100.0**
	Float-1	5.3	0.09	1.8	40.48	9.8	92.00	9.8	5.00	0.6
	Float-2	16.2	0.06	3.9	41.38	30.7	94.05	30.7	2.63	1.0
	Float-3	21.1	0.09	7.0	40.56	39.2	92.18	39.2	3.25	1.7
9	Float-4	14.1	0.51	27.9	27.67	17.8	62.89	17.8	25.88	8.9
	Float-5	13.5	0.69	36.2	1.17	0.7	2.66	0.7	79.60	26.2
	Sink	29.7	0.2	23.1	1.29	1.8	2.93	1.8	84.63	61.5
	Total	**100.0**	**0.26**	**100.0**	**21.87**	**100.0**	**49.71**	**100.0**	**40.95**	**100.0**
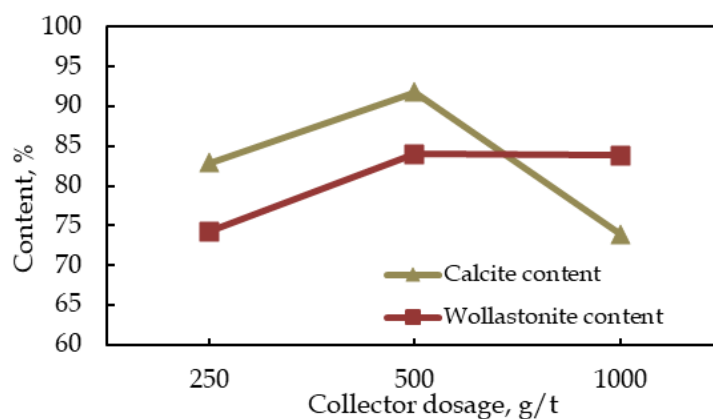
Fig. 9. Graphical demonstration of the collector dosage experiment

Table 7. Result of collector dosage experiments

Lankropol dosage (g/t)	Product	Weight %	Fe$_2$O$_3$		Loss of ignition		Calcite		Wollastonite	
			C	D	C	D	P	D	P	D
250	Float-1	5.9	0.11	2.4	35.56	9.2	80.82	9.2	15.93	2.3
	Float-2	9.1	0.12	4.0	36.88	14.7	83.82	14.7	14.08	3.1
	Float-3	11.5	0.09	3.8	36.62	18.4	83.23	18.4	13.67	3.8
	Float-4	13.4	0.07	3.5	38.81	22.9	88.20	22.9	8.52	2.8
	Float-5	14.6	0.23	12.4	34.18	21.9	77.68	21.9	17.43	6.2
	Sink	45.5	0.44	73.9	6.46	12.9	14.68	12.9	74.30	81.9
	Total	**100.0**	**0.27**	**100.0**	**22.81**	**100.0**	**51.84**	**100.0**	**41.26**	**100.0**
500	Float-1	9.9	0.11	3.5	40	18.2	90.91	18.2	5.20	1.2
	Float-2	12.9	0.14	5.7	41.54	24.6	94.41	24.6	3.40	1.1
	Float-3	22.8	0.15	10.9	39.91	41.8	90.70	41.8	5.35	2.9
	Float-4	12.3	1	39.1	22.33	12.6	50.75	12.6	35.47	10.5
	Float-5	8.9	0.81	23.0	1.69	0.7	3.84	0.7	82.10	17.6
	Sink	33.1	0.17	17.9	1.35	2.1	3.07	2.1	84.05	66.8
	Total	**100.0**	**0.31**	**100.0**	**21.78**	**100.0**	**49.49**	**100.0**	**41.72**	**100.0**
1000	Float-1	30.8	0.1	10.0	40.23	54.7	91.43	54.7	5.18	4.0
	Float-2	23.4	0.22	16.8	36.55	37.9	83.07	37.9	12.10	7.0
	Float-3	13.9	1.09	49.3	8.71	5.4	19.80	5.4	64.67	22.3
	Float-4	11.3	0.32	11.8	1.37	0.7	3.11	0.7	83.27	23.4
	Float-5	8.9	0.22	6.4	1.06	0.4	2.41	0.4	84.77	18.8
	Sink	11.7	0.15	5.7	1.85	1.0	4.20	1.0	83.83	24.4
	Total	**100.0**	**0.31**	**100.0**	**22.61**	**100.0**	**51.38**	**100.0**	**40.21**	**100.0**

C:Content, D:Distribution, P:Purity

and a pH of 6. It can be seen that wollastonite concentrate has a purity of 80% but the iron content is 0.44%. In calcite concentrate, 99.8% purity was achieved (Bulut et al., 2019). In the study conducted with Lankropol OPA, a higher purity and lower iron content in the wollastonite concentrate was obtained, although the amount of collector decreased. Unlike our study, Marchevskaya et al. (2017) applied X-ray luminescence before magnetic separation and flotation. Although they applied one more enrichment method, they produced wollastonite concentrate with a purity of 86.4%, which is only 2% more than ours.

3.3.4. Cleaning flotation

After optimizing the size, pH and collector dosage, the cleaning stage was applied for the first three floated products. The pH was kept constant during the experiment and no collector was added. The results of the cleaning stage are given in Table 8.

Table 8. Result of calcite cleaning flotation experiment.

Product	Weight %	Fe$_2$O$_3$		Loss of ignition		Calcite		Wollastonite	
		C	D	C	D	P	D	P	D
Float	43.2	0.05	26.9	42.14	44.6	95.77	44.6	2.7	21.3
Middling	35.7	0.1	44.4	39.57	34.6	89.93	34.6	8.63	56.3
Sink	21.0	0.11	28.8	40.24	20.7	91.45	20.7	5.83	22.4
Total	**100.0**	**0.08**	**100.0**	**40.82**	**100.0**	**92.78**	**100.0**	**5.48**	**100.0**

C:Content, D:Distribution, P:Purity

The calcite concentration was increased by appriximately 3%, as seen in Table 8. Aside from the rising calcite concentration, the iron content reached quite low levels. The values obtained from the cleaning stage are appropriate for calcite applications in industry.

4. Conclusions

In the context of this work, magnetic separation and flotation were used to produce calcite concentrate with marketable concentrations and wollastonite with reduced iron content. Lankropol OPA was used as a collector in the flotation applied after magnetic separation. Oleate is a type of fatty acid collector, while Lankropol OPA is a type of fatty acid sulfonate. When comparing the studies, it was found that the use of Lankropol OPA instead of oleate reduced the amount of reagents. Prior to flotation, magnetic separation was attempted, to reduce the iron content of the ore but it was found that this separation, performed in narrow size groups, was not applicable to large sizes. This could be because liberalization decreases. In the ore for which zeta potential measurements were also made, the experiments resulted in an increase in the SiO_2 content (from 28 to 84%, using 500 g/t Lankropol at pH 8 and a particle size of 100 microns) and a decrease in the iron concentration (from 0.45 to 0.17%). Additionally, the product that floated in the first three stages had a high calcite content and underwent a cleaning stage which increased its composition to 95%. Based on these findings, it can be concluded that the amount of iron-bearing waste produced by this procedure is fairly low. In conclusion, even though iron grades are adequate for several areas, the wollastonite concentrate is only ideal for metallurgical grades after analyzing the purity values. Besides, calcite is found in many other areas. The calcite and wollastonite produced can be used to make a variety of compounds or salts. For instance, both wollastonite and calcite can be used to produce $CaCl_2$ (Türk et al., 2021; Zhang et al., 2010). A cleaning circuit can also be used to prepare wollastonite for other uses.

Acknowledgments

References

AL MAHROUQI, D., VINOGRADOV, J., JACKSON, M.D., 2017. *Zeta potential of artificial and natural calcite in aqueous solution.* Adv. Colloid Interface Sci. 240, 60-76.

BULATOVIC, S. M., 2005. *Handbook of flotation reagents: Chemistry, theory and practice: Flotation of industrial minerals.* Boston: Elsevier B.V.

BULUT, G., AKÇIN, E. S., KANGAL, M. O., 2019. *Value added industrial minerals production from calcite-rich wollastonite.* Gospod. Surowcami Min. 35.

CHEN, Z., WANZHONG, Y., YIMIN, Z., ZHONGMING, W., QIAOBIN, X., 2020. *Study on the mechanism of floatability differences between calcite and wollastonite.* Conservation and Utilization of Mineral Resources, 40(4), 82-88.

ÇINKU, K., İPEKOĞLU, B., TULGARLAR, A., 1997. *Karaköy Vollastonit Cevherinin Zenginleştirilmesi.* Industrial Raw Materials Symposium. 86-91.

DPT, 2001. *Genel Endüstri Mineralleri I.* Madencilik Özel İhtisas Komisyonu Raporu, Endüstriyel Hammaddeler Alt Komisyonu, Sekizinci Beş Yıllık Kalkınma Planı, 53-58.

GAO, Z., LI, C., SUN, W., HU, Y., 2017. *Anisotropic surface properties of calcite: A consideration of surface broken bonds.* Colloids Surf. A Physicochem. Eng. Asp. *520*, 53-61.

HANER, S., ÇUHADAROĞLU, D., 2013. *Vollastonit: Bir Gözden Geçirme.* Jeoloji Mühendisliği Dergisi. 37(1), 63-82.

MARCHEVSKAYA, V.V., TERESHCHENKO, S.V., BARANOVSKY, A.F., BELUZHENKO, E.V., RUKHLENKO, E.D., 2017. *Wollastonite Concentrate Production from Raw Material of Tyrnyauz Deposit.* Fiziko-Tekhnicheskie Problemy Razrabotki Poleznykh Iskopaemykh, 3, 175–181.

MTA, nd. *Wollastonite.* Received from: https://www.mta.gov.tr/v3.0/bilgi-merkezi/wollastonit

OELKERS, E., GOBULEV, S., CHAIRAT, C., POKROVSKY, O., SCHOTT, J., 2009. *The surface chemistry of multi-oxide silicates.* Geochimica et Cosmochimica Acta. 73(16), 4617-4634.

RAVI, B., KRISHNA, S., PATIL, M., KUMAR, P., RUDRAPPA, C., NAGANOOR, P., 2014. *Beneficiation of a wollastonite from Sirohi, Rajasthan.* International Journal of Innovative Science, Engineering and Technology, 1(4), 450-453.

ŞAHİN, N. 2008. *Kalsit Hakkında Bazı Bilgiler.* Madencilik Bülteni, July-August, 48-51.

TURK, T., UCERLER, Z., BURAT, F., BULUT, G., KANGAL, M.O., 2021. *Extraction of potassium from feldspar by roasting with CaCl2 obtained from the acidic leaching of wollastonite-calcite ore.* Minerals, 11(12), 1369.

ZHANG, J., ZHANG, R., GEERLINGS, H., BI, J., 2010. *A novel indirect wollastonite carbonation route for CO2 sequestration.* Chem. Eng. Technol, 33, 1177–1183.