Value added industrial minerals production from calcite-rich wollastonite

Introduction

Wollastonite is an important industrial mineral used in the production of materials such as: ceramics, plastics, metallurgy and paint and coating materials. Wollastonite is named after W.H. Wollaston (1776–1828), an English chemist and mineralogist. It is a calcium metasilicate with the chemical formula CaSiO₃. Wollastonite is the only naturally occurring, nonmetallic, white mineral that is needle-shaped in crystal habit. This crystal habit and the mineral’s chemistry are the main reasons for wollastonite’s rise in commercial use, which began in the 1970s and has continued to the present day. Due to its high chemical and thermal resistance and nontoxic properties, wollastonite is used to replace asbestos. Due to its unique properties, it is used as a filling material for ceramics, plastics and paints, as a thermal and electrical insulator, wetting agent and metal smelter for glaze (Kogel et al. 2006). Worldwide consumption of wollastonite has significantly increased over the years, and world production was about 366,000 tons in 1990, it had risen to approximately 770,000 tons by 2017. The main markets for wollastonite are ceramics, plastics, as an asbestos substitute, metallurgy, paints and coatings (U.S. Geological Survey 2018).
Mechanical sorting, dry or wet magnetic separation and flotation are the three main methods for the beneficiation of wollastonite ore. Magnetic separation and flotation can be applied together in some cases. Mechanical sorting can be applied if the wollastonite is formed in large crystal ores. Wollastonite is, in such a case, separated from the host rock by hand sorting. The wollastonite separated by this method is marketed in lump form. The hand sorting method is used in some operations in Finland, China and Romania. Wet magnetic separation was used on several deposits from New York in the US. Diluted finely ground wollastonite was fed into a high intensity oscillating wet magnetic separator of special design and more than 90% concentrate of wollastonite showing a crystal purity of 99% was obtained. It was ground and classified to the desired product. Generally, if the ore contains garnet, dry magnetic separation is used. The ore is crushed up to 16 mesh by using a roll crusher in the study. The crushed ore is screened into three size fractions and high intensity magnetic separation is applied. After this process, high-grade wollastonite is produced using this method (Bulatovic 2005).

It is difficult to separate wollastonite from gangue minerals with selective flotation due to the needle-like crystal structure of wollastonite. Generally, reverse flotation is applied. Research was performed by the SAIGIMS Russian Institute in which the ore was used, which contained about 70% wollastonite, a 20% mixture of feldspar and 7% pyroxene with minor amounts of quartz and calcite, was beneficiated by using reverse flotation. Firstly, calcite flotation was performed by using tallow soap or saponified naphthenic acid collector in alkaline conditions, then the calcite tailing was treated with sulfuric acid. After the calcite tailing treatment, feldspar was floated using the collector ANP-14 (amine). Pyroxenes were separated using a soap collector together with 600 g/t lead nitrate as an activator. This method obtained a concentrate with 92% wollastonite content at 81% recovery (Bulatovic 2005).

Another study was carried out by the Romania Research Institute. Ore containing diopside, garnet and epidote and iron-containing ore were used in the study. In the iron-containing ore separation, firstly single-stage magnetic separation was applied, then reverse gangue flotation was performed using a sulfate soap collector. In this method, wollastonite with a 95% content at 86% recovery was obtained.

Reverse gangue flotation was performed in the ore containing diopside, garnet and epidote,. The ground ore was conditioned with sulfuric acid to pH 6–6.5, then the gangue minerals were floated using the sulfate soap collector (sodium dodecyl sulfate, etc.). If the ore contained mostly calcite with some quartz and iron silicate, the ground ore was first conditioned with fatty acid then calcite flotation was performed. After the calcite tailing was deslimed, silicate flotation was performed using a mixture of an anionic and cationic collector (Bulatovic 2005).

Another study was performed with low-grade wollastonite samples from Sirohi, Rajasthan. Flotation and magnetic separation were used together. In the flotation methods, the best results were obtained with ~150 mesh particle size, using 1 kg/t sodium oleate at pH 7. The product obtained optimum flotation conditions with 95% wollastonite, 2.64% Fe₂O₃ and 0.4% loss on ignition contents. Then, the obtained flotation product was beneficiated
with wet high-intensity magnetic separation (WHIMS) at 18000 Gauss intensity in order to remove iron minerals. The product obtained from WHIMS included 97% wollastonite, 0.49% Fe₂O₃ and 0.45% loss on ignition content (Ravi et al. 2014).

The zero point of charge (ZPC) of such minerals is low, in the range of pH 2. Wollastonite is a framework silicate and hence the ZPC should be in the same order of pH 2, like quartz and other silicates (Mi et al. 1994).

Prabhakar et al. (2003, 2005) studied wollastonite flotation with an amine type collector. They found that at low pH values, the flotation of wollastonite is worse because it possesses only a slightly negatively charged surface and hence the tendency for diamine ions to accumulate within the electrical double layer is small. As the pH of the solution is raised, the wollastonite surface becomes more and more negatively charged and more diamine ions are attracted electrostatically to the mineral surface and hence there is more flotation (Prabhakar et al. 2003, 2005).

Another study on wollastonite was done by Çinku et al. (1997). Experiments were carried out in order to reveal the availability of Karaköy wollastonite ore containing 47.56% SiO₂, 39.86% CaO, 1.33% Fe₂O₃ and 1.04% loss on ignition in the ceramic industry. Initially, a size reduction process was done using a crusher and mill for magnetic separation. The material ground to below 0.3 mm was fed to a Boxmag type high intensity disc magnetic separator. Some parameters such as the disk height, magnetic intensity, band rotation speed and feed rate were optimized. The best conditions were determined at a 2 mm disk height, 17000 Gauss magnetic field strength, and 5 rev/min band rotation speed. As a result of magnetic separation, the Fe₂O₃ content was reduced from 1.33% to 0.24%. The concentrate obtained from magnetic separation had a high loss on ignition due to containing free calcite. Therefore, reverse flotation was performed to concentrate the wollastonite. When the wollastonite was depressed, calcite was floated. During the flotation experiments, the pH, type of collector (oleoylsarcosine and oleic acid), amount of collector and solid ratio in pulp parameters were investigated. A pH regulator (caustic soda) and depressant (sodium silicate) were used in the flotation experiments. As a result of the flotation experiments, 1000 g/t of collector, pH 10.5, 1.7 kg/t of sodium silicate, and 500 g/t of caustic soda were determined as the best conditions for the two types of collector. In an experiment with oleic acid, concentrate containing 54.43% SiO₂, 41.44% CaO, 0.59% Fe₂O₃ and 0.97% loss on ignition was obtained. Another concentrate using oleoyl sarcosine contained 57.10% SiO₂, 40.88% CaO, 0.30% Fe₂O₃ and 0.13% loss on ignition. Wollastonite used in the ceramic industry should have a minimum 49% SiO₂ and 43–45% CaO, maximum 0.25–0.50% Fe₂O₃, and a maximum 1.5–4% loss on ignition. All the components of the two concentrates obtained except CaO were determined as suitable for the ceramic industry. At the end of the study, it was stated that when quartz flotation was applied to these concentrates, the CaO percentage reached the usability level (Çinku et al. 1997).

The aim of the current investigation is to produce a wollastonite concentrate for industrial applications, with the possibility of generating calcite based co-products.
1. Material and methods

The representative calcite-rich wollastonite ore sample used in this study was obtained from the Buzlukdağ deposit, Kırşehir-Akpınar region in the middle of Anatolia. The chemical composition of the sample was established using the X-ray Fluorescence (XRF) technique. Table 1 shows the chemical composition of the calcite-rich wollastonite ore sample.

Table 1. Chemical composition of examined calcite-rich wollastonite ore

<table>
<thead>
<tr>
<th>Component</th>
<th>Content (wt%)</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>41.00</td>
</tr>
<tr>
<td>CaO</td>
<td>49.01</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.56</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.21</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.34</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.73</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.20</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>28.00</td>
</tr>
</tbody>
</table>

Modular mineralogy analyses were performed with the FEI MLA 650F device, SEM (Scanning Electron Microscope) assisted image (BSE—back-scattered electron) analysis was carried out with the Bruker 5010 SDD device. The results are given in Figure 1 and Figure 2.

X-ray Diffraction analyses were carried out using a Cu X-ray-sourced Panalytical X'Pert Pro diffractometer. PDF4/ Minerals ICDD database software was used for mineral identification. Crystal mineral phases were determined using the Rietveld method. The XRD curve is given in Figure 3.

The minerals and contents of the calcite-rich wollastonite ore are given in Table 2 as the result of modal mineralogical analysis performed with XRD, SEM and EDS analyses.

The mineralogical analysis of the sample shows that the ore sample contains 55.82% wollastonite (CaSiO₃), 4.05% augite (Ca,Na)(Mg,Fe,Al)(Si,Al)₂O₆, 35.93% calcite (CaCO₃) and trace amounts of other minerals. According to the analyses, it is thought that iron may come mostly from the augite.

In the flotation experiments –300, –200 and –100 µm sized samples were used. A wet grinding method in a ceramic mill was applied for size reduction. In the grinding process, the solid ratio in the pulp was adjusted to 65% and the ball mill charge was used at 40%. The particle size distributions curves of calcite-rich wollastonite ore in original form and with different sizes are shown in Figure 4.
Fig. 1. Image analysis of examined calcite-rich wollastonite ore

Rys. 1. Analizy obrazu badanej próbki surowca przemysłowego

Fig. 2. BSE images of examined calcite-rich wollastonite ore

(thes particle sizes of all the minerals were determined as between 40–100 μm)

Rys. 2. Obrazy BSE badanej próbki surowca przemysłowego

(wielkości cząstek zawierała się w przedziale 40–100 μm)
When the particle size distribution of the original ore under 2 mm was examined, the dimension of $d_{80}$ was found as 1.2 mm; the sizes of $d_{80}$ of the materials reduced to –300, –212 and –100 microns were calculated as approximately 200, 140 and 80 microns, respectively.

The reverse flotation method was used in the selective separation of wollastonite and calcite. In the flotation process, potassium oleate was used as a collector and this method was applied by the addition of a collector in five stages. All the experiments were carried out in a Denver flotation machine. A 20% solid to pulp ratio was used in a 1.5 L volume cell at 1200 rpm flotation speed and 2 minutes flotation time. The flowsheet of the flotation experiments is given in Figure 5.

In the evaluation of the experimental studies, the wollastonite and calcite contents and yields are plotted depending on the variables; the iron oxide and loss on ignition contents for both minerals are shown in separate graphs in the following figures. In the experiments, calcite is floated in the first two stages, while the other three stages contain mainly augite, then the sinking product is obtained as a wollastonite concentrate.
Table 2. Minerals and contents of examined calcite-rich wollastonite ore

Tabela 2. Zawartość mineralów w badanej próbie surowca przemysłowego

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wollastonite</td>
<td>55.82</td>
</tr>
<tr>
<td>Calcite</td>
<td>35.93</td>
</tr>
<tr>
<td>Augite</td>
<td>4.05</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>1.37</td>
</tr>
<tr>
<td>Albite</td>
<td>0.44</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>0.42</td>
</tr>
<tr>
<td>Nepheline Syenite</td>
<td>0.31</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.26</td>
</tr>
<tr>
<td>Apatite</td>
<td>0.19</td>
</tr>
<tr>
<td>Si-Al Clays</td>
<td>0.13</td>
</tr>
<tr>
<td>Sphene</td>
<td>0.06</td>
</tr>
<tr>
<td>Muscovite</td>
<td>0.04</td>
</tr>
<tr>
<td>Garnet</td>
<td>0.01</td>
</tr>
<tr>
<td>Biotite</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Fig. 4. The particle size distribution curves of examined calcite-rich wollastonite ore

Rys. 4. Rozkład wielkości cząstek badanej próby surowca przemysłowego
2. Results and discussion

2.1. Effect of particle size

The effect of the particle size was determined in the first group experiment –300, –200 and –100 μm were used in experiments in the natural pH (≈8) of the sample. Five-stage flotation was done in three different sizes and 200 g/t of potassium oleate was added to each stage. In total, 1000 g/t of potassium oleate was used for the size determination experiments. The results are given in Figure 6.

As a result of the experiments performed, three different sizes of wollastonite, high wollastonite content and low loss on ignition were obtained at –100 μm particle size. Fugen and Sivamohan studied the split flotation of calcite from wollastonite. Their experiments carried out on mixtures of coarser size fractions with the –10 μm fraction in different proportions showed that the coarser particles, in the presence of ultrafine particles, do not float as fast as they float in the absence of such particles (Fugen and Sivamohan 1990). This size is also advantageous in the commercial market because the wollastonite size used is –100 μm in industrial usages (Kogel et al. 2006). For this reason, in experiments to investigate other parameters such as the amount of collector and the pH, the particle size was kept constant.
as –100 μm. When the combined results were examined, 77.40% purity calcite concentrate was obtained with 97.30% recovery for this size.

2.2. Effect of collector concentration

Calcite-rich wollastonite ore was subjected to flotation at different collector concentrations (1000, 1500 and 2000 g/t). The results can be seen in Figure 7.

According to the results, the best wollastonite recovery and content were obtained in the experiments using 1500 and 2000 g/t potassium oleate. When the results of these potassium oleate concentrations were examined, it was found that the loss on ignition values (respectively 0.6 and 0.28%) were close to each other and when the wollastonite recovery was evaluated, high wollastonite content and recovery were obtained in the experiment using 1500 g/t potassium oleate. Unfortunately, the desired iron content (<0.5%) was not obtained in the experiments. Also, clean calcite concentrate was obtained when using 1500 g/t potassium oleate in the combined result.

Anionic collectors are most frequently used in the flotation of semi-soluble salt minerals such as calcite. In particular, carboxylic acids are used extensively. In most instances, collector adsorption in these systems involves chemisorption. This phenomenon results from the stability of most multivalent cation carboxylate salts and the moderate solubility of the semi-soluble salt minerals (Fuerstenau et al. 1985). On the other hand, the adsorption of the silicate minerals by the collectors is due to the electrostatic attraction forces (Fuerstenau and Pradip 2005; Crundwell 2016). The zero point of silicate minerals such as wollastonite...
is between pH 2–3. Thus, wollastonite was not floated with an anionic collector because the surface charge of the mineral is negative to the working pH. Therefore, according to the stepped flotation test results, it is understood that while the calcite concentration is obtained in the first stages, the wollastonite mineral remains in the flotation cell.

### 2.3. Effect of pH

Experiments were carried out at the natural pH of the sample (≈ 8) when the particle size and amount of potassium oleate were determined. Experiments on the pH values were done at pH 4, 6 and 10, as well as the natural pH. In the experiments, the particle size was kept constant as -100 µm with 1500 g/t of collector dosage. Sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were used to adjust the pH values. The results are given in Figure 8.

From the pH-related experiments, good results were obtained at pH 6 and pH 10. The desired iron content of less than 0.5% in wollastonite product was obtained in the experiment conducted at pH 6. At pH 10, it was observed that calcite floated well due to the low loss on ignition in the wollastonite concentrate (0.19%). It was found at a natural pH that clean calcite concentrate was obtained from the combined results, with an 84.90% calcite content and 91.4% recovery.

In this study, calcite-rich wollastonite ore from Buzlukdağ, Kirşehir was beneficiated with reverse flotation. The effects of the particle sizes, collector concentration and pH were investigated in the experiments. By the gradual addition of the collector, it was found...
that wollastonite and calcite were separated successively. Calcite was concentrated in the first two stages after a couple of cleaning stages depending on the collector concentration. Iron-bearing minerals, mainly augite, were taken from the other three stages. Then, the sunken product was wollastonite. The flowsheet of this experiment is given in Figure 9.

An iron-containing product (mainly augite), which constitutes 20% by weight of the feed material, was obtained as a result of the final enrichment. This product contains about 80% purity wollastonite. This product, with an Fe$_2$O$_3$ content of 1.85%, can be used in the metallurgical industry by blending to lower the Fe$_2$O$_3$ content. Thus, a zero-waste process flow diagram can be generated.

A large loss on ignition in wollastonite concentrate was obtained at pH 10 because calcite was floated well in the first two stages with potassium oleate, which is a fatty acid type collector (Atak 2017). On the other hand, pH 6 is suitable for activating iron-bearing minerals which are silicate type, such as augite. When all the experimental results were evaluated, the best result was obtained at pH 6, and 1500 g/t amount of K-Oleate –100 mm.

Besides, the ultimate calcite concentrate obtained as another product from the experimental studies has a 99.80% calcite content and 85.4% recovery. The calcite produced contained 55.89% CaO, 0.35% SiO$_2$, 0.03% Fe$_2$O$_3$ and 42.30% LOI. This ultimate product is suitable for use in different industrial markets such as: paints, paper, plastics, detergent, poultry, refractories, electrodes, and fire extinguishers. On the other hand, a wollastonite concentrate was obtained with 52.71% SiO$_2$, 44.65% CaO, 0.44% Fe$_2$O$_3$ and 0.60% LOI. This concentrate can be used in different industrial applications such as: metallurgy, ceramics and fillers.
According to the results obtained in this study, it is possible to obtain a clean calcite concentrate as well as the wollastonite concentrate suitable for industrial use as a result of multi-stage flotation.

**Conclusions**

The production and consumption of wollastonite are increasing day by day due to the absence of a carcinogenic effect and the numerous advantages that it gives to products in many industrial markets.

Due to problems in the enrichment of high calcite content of the wollastonite ore, the evaluation of such complex ore is rather important. This study explains flotation techniques for the separate concentration of wollastonite and calcite from Middle Anatolia deposits.
However, iron-bearing minerals in this deposit (mainly augite) were also discarded in the same circuit. The operating conditions to be adopted for the design of the best final circuit were then identified. The main operating variables covered were particle size, collector concentration and pH values.

REFERENCES


VALUE ADDED INDUSTRIAL MINERALS PRODUCTION FROM CALCITE-RICH WOLLASTONITE

Keywords
wollastonite, calcite, flotation, industrial minerals

Abstract
The worldwide consumption of wollastonite has been increasing from day to day. It is a calcium metasilicate with the chemical formula CaSiO$_3$. Wollastonite is the only naturally occurring, non-metallic, white mineral that is needle-shaped in a crystal habit. Due to its high chemical and thermal resistance and nontoxic properties, wollastonite replaces asbestos. Apart from this, the acicular property of wollastonite allow it to compete with other acicular materials where improvements in dimensional stability, flexural modulus and heat deflection are sought. Due to its unique properties such as: its high brightness and whiteness, low moisture and oil absorption, low volatile content, and acicular properties, it is used also as a filling material for ceramics, plastics and paints, thermal and electrical insulator, wetting agent and smelter for glaze. Three methods are used for the beneficiation of wollastonite: mechanical sorting, dry or wet magnetic separation and flotation. Magnetic separation and flotation can be applied together in some cases. In this study, flotation has been investigated for the selective separation of calcite-rich wollastonite ores from the Buzlukdağ deposit, in the Kırşehir-Akpınar region, in the middle of Anatolia. The mineralogical analysis of the sample used in the study shows that the ore sample contains 60–62% wollastonite (CaSiO$_3$), 4–5% augite (Ca,Na)(Mg,Fe,Al)(Si,Al)$_2$O$_6$, 30–32% calcite (CaCO$_3$) and minor amount of other minerals. As a result of this study, the wollastonite concentrate which contains 0.44% Fe$_2$O$_3$, 52.71% SiO$_2$, 87.85% wollastonite with 0.60% loss on ignition (using 1500 g/t potassium oleate) was obtained. The ultimate grade concentrates of calcite that can also be obtained as by-products are with 99.80% calcite content and 85.4% recovery.
właściwości, takie jak: wysoka jasność i biel, niska wilgotność i absorpcja oleju, niska zawartość części lotnych i właściwości igielkowe, umożliwia zastosowanie jego jako: materiału wypełniającego do ceramiki, tworzyw sztucznych i farb, izolatora termicznego i elektrycznego, środka zwilżającego i pieca do glazury. Do wzbogacania wollastonitu stosowane są trzy metody: sortowanie mechaniczne, separacja magnetyczna na sucho lub mokro oraz flotacja. W niektórych przypadkach można zastosować zarówno separację magnetyczną, jak i flotację. W tym artykule zastosowano flotację w celu selektywnego oddzielenia rud kalcytu i wollastonitu ze złóż Buzluukdağ w regionie Kırşehir-Akpınar w centrum Anatolii. Analiza mineralogiczna próbki użytej w badaniu pokazuje, że próbka rudy zawiera 60–62% wollastonitu (CaSiO$_3$), 4–5% augitu (Ca, Na)(Mg, Fe, Al)(Si, Al)$_2$O$_6$, 30–32% kalcytu (CaCO$_3$) i niewielką ilość innych minerałów. W wyniku tych badań uzyskano koncentrat wollastonitu, który zawiera 0,44% Fe$_2$O$_3$, 52,71% SiO$_2$, 87,85% wollastonitu przy stratach wynoszących 0,60% (przy użyciu 1500 g/Mg oleinianu potasu). Końcowe koncentraty kalcytu, które można również otrzymać jako produkty uboczne, zawierają 99,80% kalcytu i 85,4% odzysku.