BENEFICIATION OF A WOLLASTONITE MINERAL

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ABSTRACT

In the paper are reported the results of the first stage of tests performed to verify the possibility of beneficiation of a wollastonite mineral (calcium metasilicate, CaSiO₃). The studied ore comes from a mineralized body located in the southern part of Sardinia (Italy), in the area named "Gutturu Is Abis". The mineralized body is composed of wollastonite associated with limestone, garnets and silica. The approach to the problem has consisted of grinding tests followed by flotation tests to separate the wollastonite from the gangue minerals, mainly calcite. The effectiveness of the various steps of testing was verified by comparing the results obtained with the specifications required by the wollastonite market, which impose minimum quantities of contaminants, such as iron, titanium and magnesium, while being less severe regarding SiO₂ and CaO contents. In consideration of the rather high content of calcite present in the feed material and of its better floatability compared to wollastonite, we first proceeded to its direct flotation, using as collector an industrial olein in aqueous emulsion. Sodium silicate in aqueous solution was used as a depressant. The best flotation results were obtained at basic pH values. A Denver laboratory flotation cell was utilized to perform the tests. Starting from an alimentation with a wollastonite content of 73.65%, the flotation process employed resulted in a product with 81.31% wollastonite.

Keywords: wollastonite, froth flotation, comminution

INTRODUCTION

This paper reports the results of the first phase of treatment tests carried out to verify the possibility of beneficiation of a wollastonite mineral, with the final purpose of obtaining products of such quality as to satisfy the specifications imposed by the market. The sample of mineral studied comes from a mineralized body located in the south-west of Sardinia in the region of Oridda (Monte Auseddu), which has already been the subject of investigations, with geological surveys and drillings, carried out in order to highlight the mining potential. In the investigated area, called "Gutturu is Abis", the mineralization is very irregular with a lenticular appearance. The encasing rocks consist of shale and the mineralized body is made of wollastonite in association with limestone, garnets and silica. These first steps of study on the possibilities of beneficiation of the ore consisted in the execution of several grinding and flotation tests, using different reactives. The effectiveness of the various tests was evaluated by comparing the results obtained with the specifications required by the wollastonite market, which impose

limits regarding both SiO₂ and CaO content and the presence of polluting elements such as iron, titanium and magnesium [1], [2].

MATERIALS AND METHODS

Wollastonite is a calcium metasilicate (CaSiO₃). In its pure state it has the following theoretical composition: CaO = 48.3% and $SiO_2 = 51.7\%$. Calcium is often replaced by copper, magnesium or manganese. Commonly occurring as associated minerals are diopside, tremolite, idocrase (vesuvianite), grossularia and andradite. Wollastonite is generally found in silicified metacalcars that have undergone regional metamorphism or localized volcanic activity. It in its pure state exhibits the properties summarized in Table 1 [3]:

Table 1 - Characteristics of wollastonite.

| Hardness (Moh's scale) | 4.5/5 |
|------------------------|---|
| Density | 2.80/3.09 |
| Melting point [°C] | 1,540 |
| Moisture content | 4% max |
| Index of refraction | 1.616/1.631 |
| Crystalline system | monoclinic |
| Form and habit | Sharp, fibrous, radiating mass of crystals with transparent or translucent appearance |

When pure the mineral is white, however, it can take on gray and brown coloration, due to the presence of impurities [4], the nature of which determines the profitability in the use of the mineral. Only a small number of countries are producers of wollastonite, among them the most important are United States, China, India, Finland, Mexico and Canada [5]. Wollastonite has become a useful base component in a variety of applications such as: ceramics, plastics, friction products, paints, adhesives, insulation materials, abrasives, and coating materials [6]. In this first phase of study, the main goal of the treatment tests was to upgrade the wollastonite ore by separating it from the gangue minerals, mainly represented by calcite, leaving to a subsequent series of tests the reduction of the content of other polluting elements such as, for example, iron. Table 2 shows an example of the main requirements imposed by the market in Italy in order to limit the presence of elements that may affect the quality of the final product, giving rise to problems regarding its use in industrial manufacturing.

Table 2 - Chemical and particle size characteristics required by the market for wollastonite.

| | Chemical specifications of wollastonite (technical | data sheet provided by Cookson Mineraria S.p.A.) |
|-------------------|--|--|
| | [%] | Particle size less than [mm] |
| SiO ₂ | 49-50 | 0.075 |
| CaO | 45-50 | 0.045 (better) |
| Al_2O_3 | 0.30 | 0.038 |
| Fe_2O_3 | <0.30 | |
| K_2O | 0.12 | |
| MgO | 1.30 | |
| Na ₂ O | 0.05 | |
| TiO ₂ | 0.02 | |
| MnO | 0.05 | |
| L.O.I. | 1-3 | |

Because of the lack of information, even in literature, available in general on the beneficiation of wollastonite, we made laboratory tests following a trial and error scheme, consisting of direct calcite flotation, feldspar flotation and quartz flotation. The flotation sample was obtained by sampling about 4 kg of the raw material taken from the mineralized deposit. The sample was sieved at 0.212 mm. The retained was reduced with a jaw crusher. The crushing product was then also sieved at 0.212 mm. The residual coarse fraction was dry grinded, in closed circuit, below 0.212 mm in a porcelain ball mill, providing for sufficiently limited grinding times so as to avoid the formation of an excessive amount of fine sizes, the presence of which would have resulted in high reagent consumption during subsequent flotation process. Tables 3, 4 and 5 show, respectively, the particle size distribution, chemical analysis and mineralogical analysis of the ground product that constitutes the feed at the following flotation tests.

Table 3 - Particle size analysis of the feed at flotation.

| Size class | Yield | Cumulative retained weight | Cumulative passing weight |
|----------------|--------|----------------------------|---------------------------|
| [mm] | [%] | [%] | [%] |
| + 0.150 | 17.95 | 17.95 | - |
| -0.150 + 0.100 | 14.15 | 32.10 | 82.05 |
| -0.100 + 0.075 | 6.98 | 39.08 | 67.90 |
| -0.075 + 0.040 | 17.41 | 56.49 | 60.92 |
| -0.040 | 43.51 | - | 43.51 |
| Total | 100.00 | | |

Table 4 - Chemical analysis of the flotation feeding.

| Size class | Yield | SiO ₂ | Al_2O_3 | Fe ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | TiO ₂ | MnO | L.O.I |
|----------------|--------|------------------|-----------|--------------------------------|-------|------|-------------------|------------------|------------------|------|-------|
| [mm] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] |
| + 0.150 | 17.95 | 50.20 | 1.50 | 1.10 | 41.00 | 0.39 | 0.08 | 0.30 | 0.09 | 0.10 | 5.20 |
| -0.150 + 0.100 | 14.15 | 45.40 | 1.50 | 1.10 | 40.70 | 0.42 | 0.09 | 0.31 | 0.09 | 0.11 | 4.80 |
| -0.100 + 0.075 | 6.98 | 49.50 | 1.50 | 1.10 | 40.50 | 0.44 | 0.08 | 0.30 | 0.10 | 0.11 | 6.10 |
| -0.075 + 0.040 | 17.41 | 50.30 | 1.50 | 0.96 | 41.70 | 0.36 | 0.07 | 0.24 | 0.06 | 0.11 | 4.90 |
| -0.040 | 43.51 | 48.80 | 1.50 | 0.90 | 42.00 | 0.42 | 0.12 | 0.26 | 0.05 | 0.12 | 6.30 |
| Total | 100.00 | 48.88 | 1.50 | 0.99 | 41.48 | 0.41 | 0.10 | 0.27 | 0.07 | 0.11 | 5.63 |

Table 5 - Mineralogical analysis of the flotation feeding.

| Size class | Yield | Wollastonite | CaCO ₃ | Quartz | Other |
|----------------|--------|--------------|-------------------|--------|-------|
| [mm] | [%] | [%] | [%] | [%] | [%] |
| + 0.150 | 17.95 | 73.50 | 9.80 | 5.00 | 10.00 |
| -0.150 + 0.100 | 14.15 | 77.90 | 5.50 | 10.00 | 5.00 |
| -0.100 + 0.075 | 6.98 | 69.00 | 12.80 | 5.00 | 10.00 |
| -0.075 + 0.040 | 17.41 | 75.10 | 9.60 | 4.50 | 10.00 |
| -0.040 | 43.51 | 72.50 | 12.60 | 5.00 | 10.00 |
| Total | 100.00 | 73.65 | 10.58 | 5.62 | 9.29 |

RESULTS

In view of the reasonably high content of calcite (10.58%) in the feed sample and its better floatability than wollastonite, it was decided to direct flotation of it, using a carboxylate collector, specifically an industrial olein (Pamak 4-Hercules/Pander Co.), in 2% aqueous emulsion. Sodium silicate in 2% aqueous solution was used as the depressant. Flotation was carried out in basic environment (pH = 9.5). A 1.2-liter Denver flotation cell, feed with 400 g of solid, was used to perform the tests. The impeller speed was set at 1,500 rpm. The conditioning time was 5 minutes. The following figure shows the flotation scheme adopted, with the quantities of reagents used in the various steps. A multi-stage scheme was chosen to better evaluate each stage's performance.

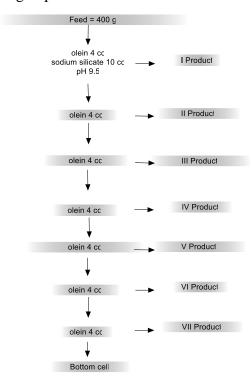


Figure 1 - Flotation scheme followed for calcite flotation.

The results, summarized in the following tables (6, 7, 8, and 9), represent the mean results of three series of tests, each performed under the same operating conditions. On the final sink material, representing the wollastonite product, a particle size analysis was performed (Table 6), and on the respective particle size classes, chemical (Table 7) and mineralogical (Table 8) analyses were performed. Table 9 shows the chemical analyses of the flotation feed, flotation products, and final tail product. It should be mentioned that some of the differences between the results reported in Table 7 compared to those in Table 9 are due to the different operating methods adopted by the two chemical laboratories used to verify the results.

Table 6 - Particle size analysis of the bottom of the flotation cell (wollastonite product).

| Size class | Yield | Cumulative retained weight | Cumulative passing weight |
|----------------|--------|----------------------------|---------------------------|
| [mm] | [%] | [%] | [%] |
| + 0.150 | 19.74 | 19.74 | - |
| -0.150 + 0.100 | 13.87 | 33.61 | 80.26 |
| -0.100 + 0.075 | 15.64 | 49.25 | 66.39 |
| -0.075 + 0.040 | 15.42 | 64.67 | 50.75 |
| -0.040 | 35.33 | - | 35.33 |
| total | 100.00 | | |

Table 7 - Chemical analysis of the final tail material (wollastonite product).

| Class | Yield | SiO_2 | Al_2O_3 | Fe_2O_3 | CaO | MgO | Na ₂ O | K ₂ O | TiO ₂ | MnO | L.O.I. |
|----------------|-------|---------|-----------|-----------|-------|------|-------------------|------------------|------------------|------|--------|
| [mm] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] |
| + 0.150 | 19.74 | 57.60 | 0.73 | 0.95 | 38.40 | 0.29 | 0.20 | 0.39 | 0.04 | 0.11 | 1.20 |
| -0.150 + 0.100 | 13.87 | 56.30 | 0.65 | 0.85 | 40.30 | 0.38 | 0.08 | 0.40 | 0.03 | 0.10 | 0.90 |
| -0.100 + 0.075 | 15.64 | 56.20 | 0.38 | 0.60 | 41.40 | 0.23 | 0.07 | 0.28 | 0.01 | 0.09 | 0.60 |
| -0.075 + 0.040 | 15.42 | 58.70 | 0.44 | 0.58 | 39.00 | 0.21 | 0.08 | 0.30 | 0.01 | 0.09 | 0.45 |
| -0.040 | 35.33 | 54.00 | 0.60 | 0.70 | 41.70 | 0.37 | 0.19 | 0.30 | 0.02 | 0.11 | 1.90 |

Table 8 - Mineralogical analysis of the final tail material (wollastonite product).

| Class | Yield | Wollastonite | CaCO ₃ | Quartz | Other |
|----------------|--------|--------------|-------------------|--------|-------|
| [mm] | [%] | [%] | [%] | [%] | [%] |
| + 0.150 | 19.74 | 76.20 | 2.90 | 4.50 | 15.00 |
| -0.150 + 0.100 | 13.87 | 81.40 | 1.70 | 10.00 | 5.00 |
| -0.100 + 0.075 | 15.64 | 84.10 | 1.40 | 10.00 | 5.00 |
| -0.075 + 0.040 | 15.42 | 79.90 | 0.72 | 15.00 | 5.00 |
| -0.040 | 35.33 | 83.50 | 2.50 | 10.00 | 5.00 |
| Total | 100.00 | 81.31 | 2.02 | 9.68 | 6.97 |

Table 9 - Chemical analysis of the flotation feed, of the floated products, of the final tail material.

| Products | Yield | SiO ₂ | CaO | Al_2O_3 | Fe_2O_3 | MgO | Na ₂ O | K ₂ O | TiO ₂ | MnO | L.O.I. |
|-------------|--------|------------------|-------|-----------|-----------|------|-------------------|------------------|------------------|------|--------|
| | % | % | % | % | % | % | % | % | % | % | % |
| Feed | 100.00 | 48.34 | 41.73 | 1.00 | 1.07 | 0.28 | 0.10 | 0.28 | 0.07 | 0.12 | 5.60 |
| I product | 2.25 | 31.45 | 44.65 | 1.00 | 0.73 | 0.28 | 0.12 | 0.19 | 0.08 | 0.13 | 20.10 |
| II product | 6.41 | 29.27 | 44.12 | 2.00 | 1.35 | 0.39 | 0.12 | 0.18 | 0.16 | 0.14 | 20.80 |
| III product | 6.92 | 33.12 | 43.71 | 2.36 | 1.63 | 0.49 | 0.13 | 0.20 | 0.18 | 0.14 | 16.46 |
| IV product | 7.00 | 36.22 | 43.56 | 2.71 | 1.89 | 0.66 | 0.13 | 0.22 | 0.18 | 0.13 | 13.00 |
| V product | 6.17 | 41.00 | 42.93 | 2.42 | 1.78 | 0.67 | 0.13 | 0.23 | 0.16 | 0.14 | 8.87 |
| VI product | 4.67 | 41.77 | 42.70 | 1.95 | 1.59 | 0.67 | 0.12 | 0.25 | 0.13 | 0.14 | 8.95 |
| VII product | 4.75 | 43.30 | 42.98 | 1.38 | 1.25 | 0.58 | 0.13 | 0.25 | 0.09 | 0.12 | 8.23 |
| Final tail | 61.80 | 51.86 | 42.16 | 0.56 | 0.91 | 0.30 | 0.10 | 0.30 | 0.02 | 0.10 | 1.75 |

The characteristics of the wollastonite product, consisting of the final tail product resulting from calcite flotation, were compared with the specifications given in Table 2. As can be seen the requirements are not completely met, in fact while the content of SiO₂ and CaO, respectively 51.8% and 42.1%, is very close to the requested value, about 50% for SiO₂ and 45% for CaO, the values, in particular of Fe₂O₃, Na₂O and K₂O, are still high. It was therefore decided to test the addition of a further phase of flotation, in order to reduce the levels of Na₂O and K₂O in the final product, by flotation of feldspars present in final tail product. For this reason, and in consideration of the use of

a cationic collector, the feed to this additional flotation stage (calcite flotation final tail) was previously subjected to a wet screening to eliminate the particle size fraction smaller than 0.037 mm, whose presence in the flotation stage could have resulted in over consumption of the collector. The sample was conditioned with hydrofluoric acid, in order to activate the feldspars, and then floated, in both acid and alkaline environments, using a primary amine as a collector.

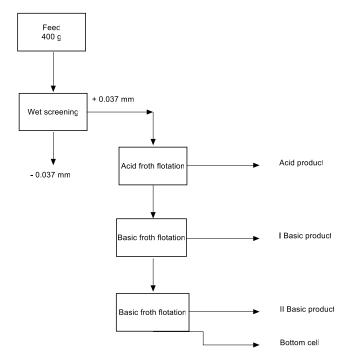


Figure 2 – Flowchart followed for froth flotation of feldspars.

Table 10 - Chemical analysis of feed to flotation of feldspars, of the products and of the final tail product.

| Products | SiO ₂ | AL_2O_3 | Fe ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | TiO ₂ | MnO | L.O.I. | Yield |
|------------------|------------------|-----------|--------------------------------|------|------|-------------------|------------------|------------------|-------|--------|-------|
| | % | % | % | % | % | % | % | % | % | % | % |
| +37µm | 56.2 | 0.60 | 0.72 | 40.1 | 0.31 | 0.086 | 0.31 | 0.025 | 0.10 | 1.3 | 64.11 |
| -37µm | 56.1 | 0.56 | 0.60 | 40.2 | 0.31 | 0.12 | 0.22 | 0.018 | 0.11 | 1.5 | 35.89 |
| Acid product | 70.9 | 1.00 | 0.65 | 25.0 | 0.26 | 0.090 | 0.60 | 0.025 | 0.070 | 1.3 | 4.77 |
| I basic product | 57.2 | 0.50 | 0.64 | 39.9 | 0.29 | 0.11 | 0.24 | 0.020 | 0.10 | 0.93 | 55.66 |
| II basic product | 56.8 | 0.55 | 0.77 | 39.6 | 0.35 | 0.11 | 0.33 | 0.024 | 0.10 | 1.3 | 17.77 |
| Final tail | 53.3 | 0.71 | 0.84 | 42.4 | 0.40 | 0.090 | 0.40 | 0.030 | 0.10 | 1.6 | 21.80 |

From the results shown in Table 10, it can be seen that the wollastonite (final tail of the feldspar flotation) represents 21.80 % of the feed, which is the grain size + 37 μ m of the final tail of Tables 7 and 9 (the + 37 μ m grain size represents 64.11 % of the final tail of Tables 7 and 9). Therefore, compared to the initial feed, the final tail product in Table 10 represents 13.98 %. The total recovery of wollastonite after this additional step is 49.87% by weight. Together with the fact that the results relative to the Na₂O and K₂O grades (Na₂O grade = 0.11%; K₂O grade = 0.27%) do not improve after the reunion of the final tail of the +37 μ m flotation with the remaining -37 μ m, previously separated by

screening, the results obtained with this flotation scheme (see table 10) are not very satisfying and have suggested the search for other alternatives. Therefore, a new series of tests developed according to the following scheme was carried out (see Figure 3): sampling of a new sample of ore and its grinding under 0.212 mm; double floatation steps of calcite, with the use of olein as a collector and quartz flotation in alkaline environment after copper sulfate (CuSO₄) addition. The latter was used to activate the quartz present in the ore, 9.68% in the final tail resulting from calcite flotation (see Table 8), allowing it to be flotated with the cationic collector used for calcite, and thus reducing the SiO₂ content of the final product.

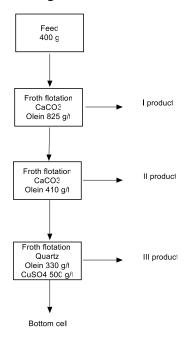


Figure 3 - Flowchart followed for froth flotation of calcite and quartz.

The applying of this alternative flowsheet also did not provide satisfactory results (see Table 11); actually, the characteristics of the obtained final tail product are little improved compared with those of the final tail sample previously obtained by calcite flotation only (see Table 7 and Table 9).

| Table 11 - | Chemical | analysis of ca | leite and au | partz flotation | products |
|------------|----------|----------------|--------------|-----------------|----------|
| Table 11 - | Chemical | anaiysis oi ca | iche and di | iaitz Hotation | moducis. |

| | | | Product | | | |
|--------------------------------|-----------|------------|-------------|--------------------|--|--|
| | I product | II product | III product | Final tail product | | |
| % | % | % | % | % | | |
| SiO ₂ | 25.2 | 33.7 | 53.3 | 53.9 | | |
| Al_2O_3 | 1.4 | 3.3 | 1.1 | 0.9 | | |
| Fe ₂ O ₃ | 0.90 | 1.9 | 1.0 | 0.9 | | |
| CaO | 50.5 | 44.4 | 41.6 | 42.8 | | |
| MgO | 0.40 | 0.50 | 0.44 | 0.36 | | |
| Na ₂ O | 0.07 | 0.09 | 0.07 | 0.07 | | |
| K ₂ O | 0.14 | 0.16 | 0.21 | 0.28 | | |
| TiO ₂ | 0.08 | 0.19 | 0.07 | 0.04 | | |
| MnO | 0.13 | 0.14 | 0.11 | 0.10 | | |
| L.O.I. | 21.1 | 11.5 | 2.0 | 1.4 | | |
| Yield | 14.75 | 10.75 | 14.00 | 60.50 | | |

From the analysis of the data obtained with the application of the different treatment diagrams, it was found that the most interesting results were obtained from the calcite flotation tests. Specifically, with the first phase, a concentrate with good characteristics, 81.31 % in wollastonite, although still in the presence above the specifications of the pollutant elements was obtained using fairly simple treatment techniques: grinding and calcite flotation.

CONCLUSIONS

The trial carried out provided evidence of the possibility of beneficiation, by means of a reverse flotation process, of a sample of wollastonite ore from the area called "Gutturu Is Abis" in southwestern Sardinia. Starting from an ore, albeit not representative of the deposit, with a wollastonite grade of 73.65%, the treatment process used resulted in a product with 81.31% wollastonite grade. The flowsheet adopted, which involves the use of flotation carried out by a classical process using carboxylic collectors in basic conditions, allowed for the almost complete removal of the carbonate gangue present. In conclusion, it can be said that the beneficiation scheme adopted makes it possible to obtain, although starting from a rather rich ore, a wollastonite product almost completely free of limestone gangue and with SiO2 and CaO contents within specifications. Therefore, it is considered opportune to pursue the study to fully meet the market specifications by reducing the content of pollutants still present in the wollastonite concentrate obtained from the flotation tests. An additional grinding step will be necessary to meet the required particle size specifications, in addition this will also result in an improvement in the degree of pollutant element liberation. The issue of reducing the content of magnetic pollutants in wollastonite remains to be addressed, regarding which it is planned to complement flotation with high-intensity magnetic separation.

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