ANALYSIS OF PROCESS OF REMOVING IMPURITIES FROM CALCIUM CARBONATE

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Abstract: Calcium carbonate is used as an additive in the production of paper and some other production processes. The aim of this study was to determine the chances of the calcite sample to be mechanically cleaned of impurities so that the material can become commercially interesting, primarily to be sold to the paper and other-related industries. A mineralogical petrographic investigation carried out on a sample of calcite showed that an unfavorable impurity is, in particular, graphite – which is otherwise fairly easily to remove with the process of flotation. A flotation procedure was performed with samples of different particle size. The purpose of this was to find an optimal particle size for carrying out the flotation. In order to achieve an effective flotation it is first necessary to achieve the proper liberation of grains. The second part of the study was to explore the optimal sequencing of treatment procedures for tested calcite, using milling, flotation, and sedimentation.

Introduction

Some of the minerals are used as additives in the production of paper and some other production processes. For instance, in paper industry some raw materials are used for coatings and as fillers. Fillers are the most significant portion of additives in this industry, in terms of percentage of weight (Gaudreault et al., 2009). Typical filler additions range from 3% to 30 % (Scott, 1996). One of these is calcium carbonate (Gronfors, 2010), which has been eagerly researched as an essential material used for industrial products over the past years (Kadota et al., 2014; Chikazawa and Fuji, 2001). White inorganic materials are added to paper to improve the printability of the surface, opacity, brightness, and the smoothness of paper (Kirwan, 2013).

Mineral resources extracted from deposits usually do not occur independently, but contain impurities in variable proportions. Impurities may affect the color of raw

material, so it is usually necessary to mechanically and chemically remove impurities before the application of useful substances.

The chemical treatment is often an environmentally unfriendly process, resulting in various unfavorable effects on the product, e.g. an unpleasant smell. Thus, it is desirable for the mineral raw material to be as mechanically cleaned of impurities as possible before going through the optional chemical treatment.

Due to differences in the composition of ore in different seams with the same mineral resource, and also because of such differences within a given deposit, it is necessary to adapt an ore preparation procedure to meet the specific requirements. We therefore need to optimize already in practice well-known technological processes, depending on the type and proportion of useful substances and impurities. This practically means that procedure, adapted to the specific requirements of the mineral resource is original process.

The aim of this study was to determine the possibility of removing some of the impurities from calcite samples with the use of mechanical cleaning methods. We were especially focused on removing graphite (Wakamatsu and Numata, 1991) in order to make the final product useful for the paper, paint, adhesives, sealants and similar industries. Other authors also acknowledge the problem of graphite occurrence in raw materials, especially its negative impact on the color of useful substances and write about ways for its removal in their articles. Raghavan et al. (1992), for instance in the article on processing kaolin contaminated with small amounts (0.1-0.3%) of graphitic impurities, reported that the beneficiation technique based on froth flotation was successfully used for the removal of ultrafine graphite particles.

Material and experimental procedures

A mineralogical and petrographic investigation was carried out on a sample of calcite, the purpose of which was to determine mineral composition of the calcite sample, with a focus on determining the presence of undesirable impurities.

The sample was used for making a standard petrographic thin section for optical microscopic analysis. The analysis of impurities was made with a scanning electron microscope (SEM) with backscattered electrons (BSE) in a high vacuum. For this purpose the surface of the sample was smooth yet not polished. A semi-quantitative chemical composition was determined on the basis of the X-ray spectra of characteristic Kα radiation at 20 kV accelerating energy (EDS-Energy Dispersive System).

The sample was homogeneous, with a uniform light gray color. Microscopic analysis showed that it was a calcite marble. The visual assessment of the quantity of non-carbonate inclusions was 2%. Practice shows that the color of the marble depends on impurities; the more impurities, the more colored they are.

The following impurities were determined in the calcite (listed with decreasing frequency): opaque minerals, especially graphite (Fig. 1), quartz, white mica,

feldspars, dolomite, titanite, chlorite, and biotite. Grains of pyrite and iron oxides were also present. Quartz, mica, iron oxides and pyrite appeared in approximately equal ratios. In the process of obtaining a suitable calcite flour it was necessary to remove the graphite, as well as Fe-oxides, and pyrite, which slightly color flour to gray when milling.
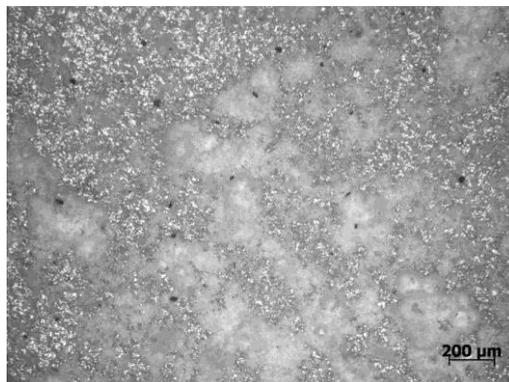
Fig. 1. Black graphite particles in calcite marble

The mineralogical petrographic analysis of the sample of calcite showed that it is necessary to pay particular attention to the removal of graphite components in calcite, as their effect on the color of calcite flour according to the properties of graphite itself and its share in the sample is dominant. Due to the fact that graphite has electrostatic properties (Taylor, 1988) the first association was electrostatic separation of graphite from the other components in the corona field.

The sample for the test with electrostatic separator mark "Krupp" was prepared in an appropriate particle size range: 0.1 to 3 mm as required by the manufacturer of the device in order to achieve the proper results. The separator should have separated the electrically conductive components of the sample from the electrical non-conductive, but we did not get the desired result. The reason for this was that the graphite particles had a diameter of only a few micrometers, and were thus at the particle size at which we wanted to separate them, still joined together with calcite. The electrostatic separator recognized most of the particles as electrically non-conductive, therefore we did not carry out further research with this equipment.

The next procedure with which we wanted to remove the graphite components out of calcite marble was flotation. This physicochemical process of separation of various minerals exploits the hydrophobic and hydrophilic properties of the separated components and is among beneficiation methods the most often used because of its superior efficiency (Drzymala, 2007; Ahmed et al., 2013). Graphite is quite hydrophobic (Du, 2008), and relatively easy to separate with the flotation. Naturally hydrophobic minerals are not easily wetted with water due to the low polarity of their

surfaces. With the appropriate reagents added the efficiency of the procedure only increases.

Before carrying out the flotation we crushed and milled calcite sample. Then analyses (Table 1) of the particle size with a Sympatec Helos H2070 particle size analyzer as well as analyses of the ISO brightness R_{457} of the samples with a Datacolor Elrepho SF450X spectrophotometer were performed.

Table 1. Particle size and ISO brightness R_{457} of the samples before the flotation

Sample	d_{50}/d_{98} (μm)	R_{457} (%)
Sample 1 (basic milling)	41.52/211.50	76.95
Sample 2 (1 min of additional milling)	26.61/189.50	76.36
Sample 3 (5 min of additional milling)	5.99/51.48	78.13
Sample 4 (15 min of additional milling)	3.69/46.92	77.42
Sample 5 (30 min of additional milling)	2.74/33.51	75.95

The flotation of graphite was carried out with the flotation cell of the type "Denver" (Fig. 2). 1.2 dm^3 of water with a pH value between 7.5 and 8 was poured in the flotation cell container. An adequate pH was achieved by the stepwise addition of NaOH and stirring. Kerosene (500 g/t) was added as a collector in the slightly alkaline water (Kaya and Canbazoglu, 2007). The kerosene and water solution was stirred for about 1 minute at 1,300 rpm, and then 150g of calcite was added. Also, a frother was added - pine oil (100 g/t) before the air vane was opened. The relatively high hydrophobicity of graphite made it possible to begin flotation immediately. Graphite particles were raised by the air bubbles to the surface and ended up in the overflow. With a frother added we achieved stable froth, eliminated the additional amount of graphite, and thus increased the efficiency of flotation.

Fig. 2. Flotation of graphite with the flotation cell "Denver"

The flotation process was performed using samples of different particle size. The purpose of this, was to find the optimal particle size for carrying out the flotation. For effective flotation it is, as in all other cases of mineral dressing, first necessary to achieve the proper liberation of grains by crushing and milling. But when the material is crushed and milled two problems arise. First, the milling of the material results in attrition between the calcite and graphite particles which consequently leads to undesired coloring of the calcite surfaces. Another problem is linked to the flotation process, more precisely to the flotation of fine grains. When floating extremely small grains the ratio between the number of air bubbles and the number of particles of the floated component is markedly in favor of the latter, and so the flotation process may not be effective. The problem of the fine particles flotation is also weak collision of the fine particles with bubbles (Sahbaz et al., 2012).

Results and discussion

After the flotation process was carried out, the samples were dried, and re-analysis of the ISO brightness followed. Before carrying out the flotation the initial samples had the R_{457} values in the range between 76% and 78%, and the minimum value was found in Sample 5 (Table 1).

Table 2. ISO brightness R_{457} of the samples after flotation

Sample	R_{457} (%)	ΔR_{457} before and after flotation (%)
Sample 1	81.81	4.86
Sample 2	82.66	6.30
Sample 3	84.94	6.81
Sample 4	86.04	8.62
Sample 5	83.97	8.02

The highest value and the greatest progress of ISO brightness R_{457} after the flotation were found in Sample 4 (Table 2). This sample had a mean particle size prior to flotation of $d_{50} = 3.69$ μm. From the ISO brightness R_{457} of samples after flotation it can be assumed that with Sample 4 an adequate liberation of grains was achieved and separating process was successfully carried out. At the same time milling was not so long-lasting that would result in excessive attrition between graphite and calcite grains and coloring of the latter.

Considering that, usually one and the same material has different optical properties with different grain sizes, flotation products were milled to a comparable size. Sample 5 with the median particle size $d_{50} = 2.74$ μm, represented the reference point and was

not milled further. Other samples were milled in two stages. The first stage lasted for 12 min and the second stage an additional 30 min.

After the first stage of milling ISO brightness improved somewhat for most samples (Table 3), which can be attributed to the emergence of new calcite surfaces. After the final milling to a comparable size, the ISO brightness had somewhat deteriorated (Table 4). The milling does, however, still open new surfaces of calcite, which improves optical properties. At the same time the liberated graphite grains cause the calcite surfaces to re-color due to attrition.

Table 3. Particle size and ISO brightness R_{457} of the samples after the first stage of additional milling (12 min)

Sample	d_{50}/d_{98} (μm)	R_{457} (%)
Sample 1	9.53/51.51	83.38
Sample 2	6.37/54.70	85.87
Sample 3	4.29/53.98	86.10
Sample 4	3.44/42.22	85.82

Table 4. Particle size and ISO brightness R_{457} of the samples after the second stage of additional milling (30 minutes, Sample 5 – no additional milling)

Sample	d_{50}/d_{98} (μm)	R_{457} (%)
Sample 1	2.85/49.31	81.33
Sample 2	2.85/51.83	80.06
Sample 3	2.55/44.72	84.02
Sample 4	2.52/42.70	83.86
Sample 5	2.74/33.51	83.97

After completing the optimization, the purpose of which was to find a suitable particle size to carry out the flotation, we wanted to check the optimal sequencing of treatment procedures for calcite sample. As shown in Fig. 3, the procedures consisted of milling, flotation, and sedimentation followed by centrifugation. Sedimentation was performed with the sample manually mixed in the water. The heavier grains first sediment to the bottom of the vessel, after that the water was removed by a centrifuge. For the further process only the top – the clean part of the sample was used, while the lower part with heavier grains such as pyrite and other iron minerals was discarded. The clean part of the sample represented approximately 80% of the initial sample. As can be seen from the scheme we also tried with a two-stage flotation.
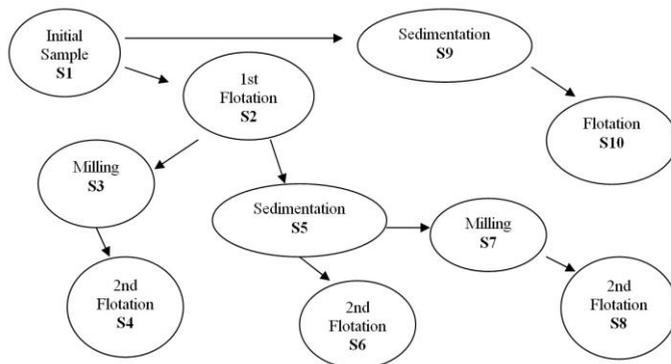
Fig. 3. Sequencing of treatment procedures

— Sample S1: initial sample
— Sample S2: floated
— Sample S3: floated, milled
— Sample S4: floated, milled, again floated
— Sample S5: floated, sedimented
— Sample S6: floated, sedimented, again floated
— Sample S7: floated, sedimented, milled
— Sample S8: floated, sedimented, milled, again floated
— Sample S9: sedimented
— Sample S10: sedimented, floated

Table 5. Particle size and ISO brightness R_{457} after completion of the cleaning procedures

	Sample									
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
d_{50} (μm)	4.16	-	2.46	-	-	-	2.56	-	-	-
d_{98} (μm)	83.74	-	29.55	-	-	-	26.87	-	-	-
R_{457} (%)	75.57	80.9	81.98	81.59	82.05	81.26	82.82	82.33	76.05	82.46

The results of the analysis (Table 5) indicate that a multi-stage flotation did not bring the desired progress of the ISO brightness of the samples. The twice floated Sample S4 didn't have higher ISO brightness than the once floated Sample S2. After the second flotation the samples had actually lower values of ISO brightness than after the first flotation. This is partly due to the impact of the reagents used for the flotation. As has already been stated, the most problematic mineral with regard to the optical properties in the tested material was graphite, so that the removal of heavy minerals with sedimentation presented much smaller progress compared to the flotation process. The Sample S9 with ISO brightness $R_{457} = 76.05\%$ showed only a minor

improvement in regard to the measured parameter in comparison to the initial Sample S1 with $R_{457} = 75.57\%$. In the case of different sequencing of the same procedures, sedimentation prior to flotation proved to be the better option – once heavy particles are eliminated, flotation is more effective than with the presence of heavy particles.

Conclusions

We wanted to mechanically clean calcite sample from impurities, particularly graphite, which was exposed in the test material as the main cause of the coloring of the calcite. The aim was examining the potential use of the tested calcite in the paper industry, as well as in industries like the paint, adhesive, and sealant. In doing so, we tried to get the highest possible level of ISO brightness, while the recovery has not been a priority concern.

At first, due to electrical conductivity of graphite, the electrostatic separation of graphite from other material was used. However, the process was not successful, because on one hand the lower limit of separating with the equipment that we have is about 100 μm, and on the other hand graphite particles in the tested material had a diameter of only a few microns.

Removal of the graphite was then undertaken using the flotation process, in which ore is separated on the basis of the hydrophobicity and hydrophilicity of the separated components. Graphite is a naturally hydrophobic, and with the addition of suitable reagents the efficiency of the process can be additionally increased.

Monitoring the process of separation of impurities from calcite was carried out by determining the ISO brightness R_{457}. The initial values of R_{457} were between 76% and 78%, while the required minimum value in the paper industry is about 94%. For the production of paints the minimum limit is approximately 90%.

Samples prepared with the different particle size were first floated, and then milled in two stages. ISO brightness R_{457} was determined for the initial sample and for the products, respectively.

The maximum value of ISO brightness R_{457} was measured in the "Sample 3" after flotation and the first stage of additional milling (initial $d_{50} = 6$ μm, $R_{457} = 86.10\%$, final $d_{50} = 4.3$ μm) as well in the "Sample 4" after flotation ($d_{50} = 3.7$ μm, $R_{457} = 86.04\%$). The maximum value of ISO brightness R_{457} among the samples, which were milled to a comparable size (about 2.7 μm), was found in "Sample 3" ($d_{50} = 2.55$ μm, $R_{457} = 84.02\%$).

The optimum particle size for carrying out the flotation with the tested material, therefore, was determined, but it may not be equal to the required particle size, which of course, depends on the intended use of material tested.

With the procedures applied we came fairly close to the minimum requirements concerning optical qualities in the aforementioned industries. Further progress in the corresponding values would be possible with the use of chemical procedures.

For comparison, Raghavan et al. (1992) in their article on processing kaolin contaminated with small amounts (0.1-0.3%) of graphitic impurities stated that the beneficiation technique based on froth flotation was successfully used for the removal of ultrafine graphite particles. The process removed around 70% of graphite, which in the case of ultra-fine particles can be considered a success.

In regards to the most economical and effective sequence of treatment procedures for the tested material, the process in which the material is first treated by the gravitational process – sedimentation and followed by the single-stage flotation proved to be most efficient. Flotation in two stages has not proven particularly effective because the graphite was already fairly well removed in the first stage of flotation.

References

AHMED, A. M. H., ALJUHANI, S. M., DRZYMALA, J., 2013, *Flotation after a direct contact of flotation reagents with carbonate particles, Part 1. Model investigations*, Physicochem. Probl. Miner. Proc., 49(2), 713−723.

CHIKAZAWA, M., FUJI, M., 2001, *Nanoparticles of lime and calcium carbonate*, J. Soc. Inorganic Mater., 8, 507-514.

DRZYMALA, J., 2007, *Mineral Processing. Foundations of Theory and Practice of Minerallurgy*, Oficyna Wydawnicza PWr., Wroclaw, http://www.dbc.wroc.pl/Content/2070/Drzymala.pdf.

DU, H., 2008, *Flotation chemistry of selected alkali halide salts and naturally hydrophobic minerals: a molecular dynamics simulation study*, PhD. Thesis. University of Utah, http://books.google.si/books?id=wG2thJzLnfQC&printsec=frontcover&hl=sl&source=gbs_ge_summ ary_r&cad=0#v=onepage&q&f=false.

GAUDREAULT, R., CESARE, N. D., WEITZ, D.,VEN, T. G. M., 2009, *Flocculation kinetics of precipitated calcium carbonate*, Coll. Surf. A: Physicochem. Eng. Aspects, 340, 56-65.

GRONFORS, J., 2010, *Use of fillers in paper and paperboard grades*, http://urn.fi/URN:NBN:fi:amk-2010060811766.

KADOTA, K., FURUKAWA, R., TOZUKA, Y., SHIMOSAKA, A., SHIRAKAWA, Y., HIDAKA, J., 2014, *Formation mechanism of non-spherical calcium carbonate particles in the solution using cluster-moving Monte Carlo simulation*, J .Mol. Liq., 194, 115-120.

KAYA, O., CANBAZOGLU, M., 2007, *A study on the floatability of graphite ore from yozgat akdagmadeni (Turkey)*, http://www.oredressing.net/download.aspx?T=DOC&ID=83.

KIRWAN, M. J., 2013, *Handbook of paper and paperboard packaging technology*, John Wiley & Sons, Bognor Regis, 432 pp.

RAGHAVAN, P., SIVAM, C., LALITHAMBIKA, M., DAMODARAN, A. D., 1992, *Removal of ultrafine graphite impurities from China clay by floc- flotation*, Int. J. Min. Proc., 36, 51-61.

SAHBAZ, O., ERCETIN, U., OTEYAKA, B., 2012, *Determination of turbulence and upper size limit in Jameson flotation cell by the use of computational fluid dynamic modelling*, Physicochem. Probl. Miner. Proc., 48, 533-544.

SCOTT, W. E., 1996, *Principles of wet end chemistry*, Tappi Press, Atlanta.

TAYLOR, J. B., 1988, *Dry electrostatic separation of granular materials*, http://ieeexplore.ieee.org/stamp/stamp.jsp?tp=&arnumber=25295.

WAKAMATSU, T., NUMATA, Y., 1991, *Flotation of graphite*, Min. Eng., 4, 975-982.