The Evaluation Potential as Micronized Calcite of White Marble Waste

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Abstract

Natural calcium carbonates have a great importance in the world's economy due to their numerous applications areas such as calcium carbonate in the paper and paint industries. The final calcite products have rigorous quality specifications which are currently difficult to meet for local producers in Turkey. Therefore, large quantities of high white marble wastes have been transported long distances inside the country to supply the different industrial plants for using calcite. Marble wastes, located in Afyon and Kutahya regions, Turkey's mid-west, are used generally for concrete and highway purposes.

Evaluations of marble wastes are very important for the economic development of any country or region. This study aims at developing new perspective for evaluation of marble wastes as domestic calcite resources and serves as a guide for investment and decision making for the Turkey calcite industry.

This paper presents applied research work to determining the product quality for evaluation as micronized calcite of marble wastes and gives an overview of the market situation for the regional producers. The aim of the work is to characterize four different marble wastes and to determine the potential for production of the required quality for the Turkey calcite market;- to control the quality of the products by application tests, including the measurement some tests.

Keywords: *calcite, marble wastes, micronized calcite, physical, chemical, physicochemical and mineralogical properties of micronized calcite*

Introduction

Limestone, which is composed mostly of calcite and aragonite minerals, i.e. different crystalline forms of calcium carbonate $CaCO_3$, abundant and widely distributed, comprises around 4% of the earth's crust [1]. Pure limestone ($CaCO_3$) has 56.0% CaO and 44.0% CO_2. In practice, virtually all limestone contain impurities such as organic (bituminous) constituents, clay minerals, quartz, mica, iron-bearing minerals such as limonite or pyrite, feldspar, amphibole and pyroxene [2]. Limestone is also one of the cheapest commercially available inorganic materials [3], and therefore has innumerable industrial applications: it is used in paints, inks, coatings, paper products, plastics and films [4–5]. These carbonate minerals are precursors of marbles. Marble is a metamorphosed carbonate rock with re-crystallised minerals with size range from millimetre to several centimetres.

Storage of in certain areas or random disposal of marble wastes can cause both visual pollution and cause pollution of other natural resources as come together with other elements. This economic potential, which is accumulated hundreds of thousands or even millions of tons of waste in marble quarries and factories, is also important in terms of its contribution to the country's economy by making efforts to enable it to be an industrial product material. Nowadays, studies have been carried out by many researchers in recent years about the recycling of marble wastes. These can be considered as asphalt, concrete, aggregate and joint in the construction sector, in the agricultural sector as a soil conditioner and as animal feed. However, in these sectors, calcite can be recycled as low value added. On the other hand, white marble wastes can be recycled as micronized by having much more added value. White marbles are called calcium carbonate or calcite [6].

Calcite, in other words calcium carbonate ($CaCO_3$), glass shimmering, transparent, easily breakable, has Mosh hardness 3 and a specific gravity in range of 2.6–2.8, is a large crystal marble. It is micronized by grinding then classification processes is applied, and offered to the use as natural ground or ground and coated calcite according to sectors, usually as fillers, for the ceramic, glass, paint, paper and plastic sectors. In addition, micronized calcite is also used in certain rates for toothpaste, adhesive, chewing gum, sponge, rubber, carpet base and oilcloth base. The use of calcite as a filler in papermaking permits the production of a brighter paper with a greater resistance to yellowing and ageing. In addition, when it is used as a part of the coating of the paper, it provides better opacity, printability, ink receptivity and smoothness, while its use as filler for plastics improves heat resistance and hardness [4].

There are basically three characteristics that define the quality of ground natural calcium carbonate (calcite) during use. These are the particle size, the chemical purity and the color parameters of calcite (whiteness, brightness and yellowness) in terms of optical property. Additionally, depending on the place of use; there are also sought features such as surface area, size distribution, electrochemical properties, oil absorption properties, dispersibility in solution etc. In the production of micronized calcite, the properties of marble wastes must be carefully examines to ensure that they meet the market conditions.

In this study, the potential of micronized calcite production of four different white marble wastes were investigated. For this purpose, initially, marble waste samples were

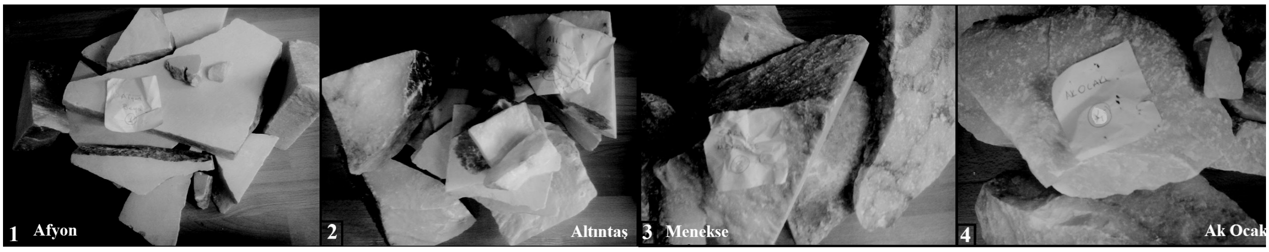

Fig. 1. General view of marble wastes used in experiments (Afyon [1], Altıntas [2], Menekse [3] and Ak Ocak [4])
Rys. 1. Widok ogólny odpadów marmurowych używanych w eksperymentach (Afyon [1], Altıntas [2], Menekse [3] i Ak Ocak [4])

Tab. 1. The results of chemical analysis by XRF of the marble wastes [*LOI: Loss on ignition]
Tab. 1. Wyniki analizy chemicznej XRF odpadów marmurowych [* LOI: Strata prażenia]

No	Sample Name	%								
		LOI*	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	K_2O	Na_2O
1	Afyon	44.01	51.30	2.75	1.34	0.21	0.15	0.19	0.06	0.00
2	Altintas	43.21	54.90	0.26	1.19	0.13	0.14	0.13	0.04	0.00
3	Menekse	41.72	50.34	0.92	1.81	0.22	4.65	0.15	0.09	0.10
4	Ak Ocak	43.39	55.77	0.24	0.42	0.03	0.01	0.09	0.01	0.03

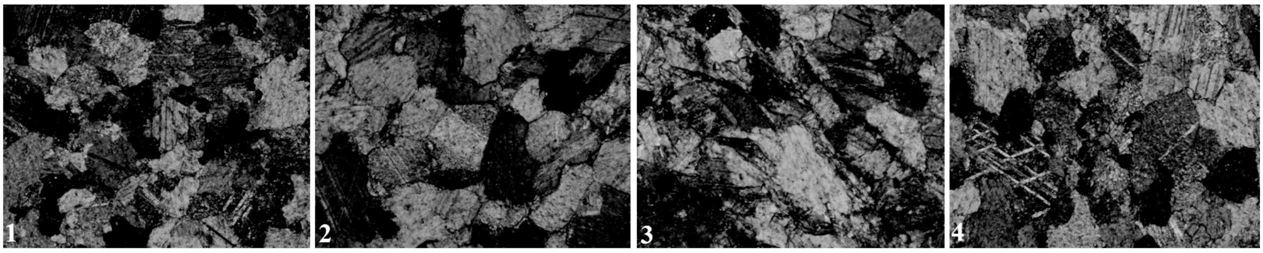

Fig. 3. Microstructure of fine crystalline marble used in experiment
Rys. 3. Mikrostruktura drobnego krystalicznego marmuru zastosowanego w eksperymencie

collected wastes from four different white marble quarries in Turkey. Then, the mineralogical, physical, chemical and physicochemical properties of the white marble wastes were investigated. According to the test results on the samples, micronized calcite obtained from four different marble wastes has been discussed whether it can be recycled according to the conditions demanded by the sector.

In this study, a comprehensive study was carried out on four different marble waste samples. These studies are listed as follows:

1. Chemical analysis (XRF),
2. Determination of rock structure (XRD),
3. Determination of mineralogical analysis (Polarized microscope),
4. Thermal Gravimetric Analysis (TGA),
5. Differential Thermal Analysis (DTA),
6. Morphological change status determinations of raw and ground samples (SEM),
7. Determination of rheological properties of samples in suspension (Viscometer),
8. Surface charge measurements of samples in suspension (Zeta meter),
9. Measurement of contact angle of samples (Contact angle meters),
10. The Bond grindability and work index determination (G_{bg} and W_i),
11. Laboratory diameter grinding and size analysis to determine the studies,
12. Determination of optical properties of ground samples by grinding (RY, R457 and YI).

Material and methods

Material

The marble samples are located at mid-west Turkey. Many marble quarries are operated in this area and they produce in huge quantity of wastes. The marble wastes used in the experiments were taken from four different marble quarries in Afyon and Kutahya region (Turkey) by the whiteness, and the samples were called as Afyon (1), Altıntas (2), Menekse (3) and Ak Ocak (4). The samples consist of marble waste fragments from 50 to 400 mm. The best quality fragments were hand-picked from the marble wastes. Figure 1 shows the names and codes of the samples with the general image.

Method

The mineralogical analyses of the marble samples were performed with a Zeiss polarized photomicroscope. Particle size distribution was conducted by Malvern laser particle size analysis equipment. The chemical analyses of the marble samples were made by XRF. The mineral composition of the marble sample was obtained by XRD. In respect to electrokinetic potential measurement of the marble samples, the surface charge (z.p.c.) was performed by Malvern zeta meter and surface tension was performed by contact angle meter. The determining of rheological properties in suspension of the marble samples was made by a Brookfield viscometer.

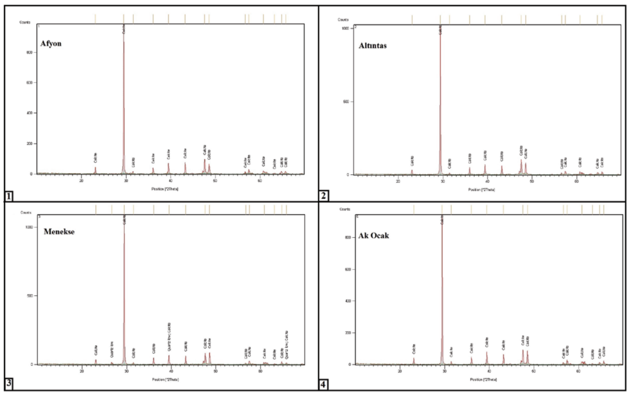

Fig. 2. The results of XRD pattern for four different marble wastes
Rys. 2. Wyniki XRD dla czterech różnych odpadów marmurowych

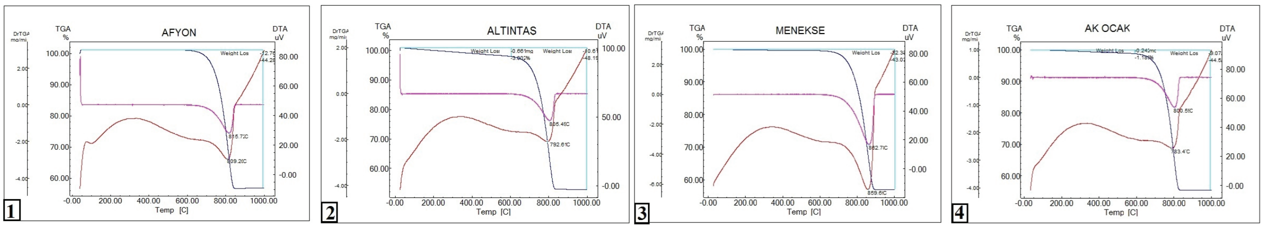

Fig. 4. TGA and DTA spectra of the marble wastes used in experiments
Rys. 4. Widma TGA i DTA odpadów marmurowych użytych w doświadczeniach

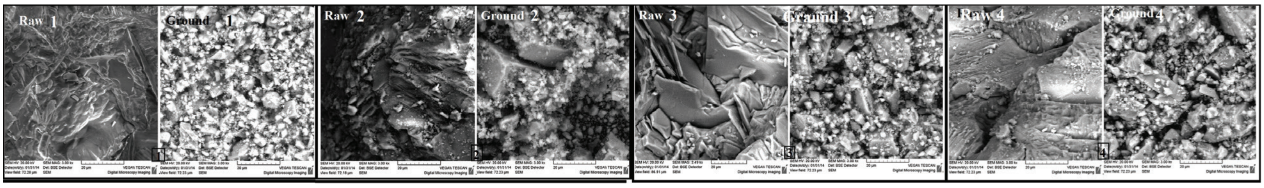

Fig. 5. SEM images of raw and ground marble wastes used in experiments
Rys. 5. Obrazy SEM surowych i zmielonych odpadów marmurowych stosowanych w doświadczeniach

The changes in the weight loss of the marble samples were determined by differential thermal analysis (DTA) and thermo gravimetric analysis (TGA). The resistance to grinding of the samples was obtained according to the Bond grindability. Optical properties (brightness, whiteness and yellowish) of the marble samples were determined by Datacolor Elrepho photoelectric spectrophotometer. SEM analyses have been made in terms of surface morphology characteristics of the raw and ground samples.

Results and Discussion

Chemical Analysis (XRF)

Each of the samples was analyzed by XRF device and the results are given in Table 1. As can be seen from the results, it is seen that all samples have high quality because of their high CaO content. In addition, low SiO_2 ratios are also important. From these data, it appears that 4 samples are suitable for the use of calcite. Specifically, sample no 2 and 4 were found to be more preferable because they had the highest $CaCO_3$ content.

Rock Crystal Analysis Studies (XRD)

To understand the rock structure, rock analysis was performed by XRD. The results of XRD for each sample that emerged in these studies are given in Figure 2. In the XRD studies, 4 samples were found to be calcite mineral. In Figure 2, a very small amount of quartz mineral was also detected in the Menekse (3) sample, but it has a little more quartz mineral than other samples. According to the results of chemical analysis (XRF), the fact that the highest SiO_2 value in the Menekse (3) sample is also support on the XRD results. From this point of view, each sample can be evaluated as calcite.

Mineralogical Analysis Studies

For a better understanding of the properties of the samples, a detailed thin section microscopic study was carried out to determine the crystal structures, the mineralogical composition and particle sizes under the polarized microscope and to reveal the advantages or disadvantages in the grinding process. In investigation by microscope indicates that all sample types consist of more than 95% carbonate mineral.

The carbonate minerals identified in the marble waste samples are calcite. The most common silicate mineral in the samples is also quartz. It is necessary to limit the content of non-carbonate impurities in high-value carbonate products because of their adverse effect on the industrial processes where the carbonate product is used, mainly due to high abra-

Tab. 2. Viscosity values (cP) for different speed of the suspensions of marble wastes used in the experiments
Tab. 2. Wartości lepkości (cP) dla różnych prędkości zawiesin odpadów marmurowych użytych w doświadczeniach

Spindle Speed	Calcite sample sold in the market	Afyon 1	Altintas 2	Menekse 3	Ak Ocak 4
(rpm)	cP	cP	cP	cP	cP
10	680.0	621.18	952,96	971.39	974.39
20	312.5	289.41	464,51	510.81	511,38
50	102.0	86.66	164.07	201.57	204.62
100	46.0	18.46	60.85	86.66	112.46

Tab. 3. Surface tension results calculated from contact angle measurements at different pH of the marble wastes used in experiments
Tab. 3. Wyniki oznaczenia napięcia powierzchniowego obliczone na podstawie pomiarów kąta zwilżania przy różnym pH odpadów marmurowych użytych w doświadczeniach

Sample No	Surface tension (dyne/cm)			
	pH			
	4.16	7.12	9.30	11.29
Afyon (**1**)	38.51	45.51	38.83	39.98
Altintas (**2**)	43.75	47.75	43.25	47.63
Menekse (**3**)	53.13	52.75	56.13	54.13
Ak Ocak (**4**)	45.02	55.25	58.99	58.38

Tab. 4. The Bond grindability (G_{bg}) and Bond work index (W_i) values of marble wastes used in experiments
Tab. 4. Wartości podatności na mielenie Bonda (G_{bg}) i wskaźnika pracy Bonda (W_i) odpadów marmurowych użytych w doświadczeniach

Sample	G_{bg} (g/rev)	W_i (kWh/t)
1 (Afyon)	2.880	8.309
2 (Altintas)	3.748	6.870
3 (Menekse)	2.870	8.575
4 (Ak Ocak)	3.340	7.209

sion in machines. According to polarizing microscopy investigations on the marble wastes, it has been determined that each sample will not cause problems in grinding process due to excessive wear or not increase energy costs.

The typical carbonate and silicate minerals microstructures observed in thin sections are shown in Figure 3. Each marble wastes are finely crystallized, with particle sizes of less than 2 mm and mean particle sizes of 0.5 mm.

As samples 1 and 3 are examined, calcite crystals are generally locked with intricate boundaries. Intricate crystal boundaries can provide stronger clamping of crystals. The intricate crystal boundaries can be more difficult to micronize during grinding. However, as samples 2 and 4 are examined, the calcite crystal size is less than 1 mm, but the cleavage surfaces in the calcite crystals are well developed. The cleavage surfaces of growing calcite crystals by re-crystallisation processes become apparent. It can be thought that this feature will contribute positively to the process of grinding the calcite crystals. The polygonal crystal boundaries can be more easily micronized during grinding.

On the other hand, when sample 3 (Menekse) is examined; the impurities such as iron (hematite), silica (quartz), graphite and mica (muscovite) were detected. Addition, sample 4 (Ak Ocak) has the impurities such as iron and graphite. These very little impurities do not complicate the grinding process, but have a negative effect on the optical properties. This situation seems to may be a problem in terms of micronized calcite minerals for similar filler use like chemistry, paint and food.

Heat Weight Loss Study (TGA and DTA)

Tests were performed with TGA and DTA devices in order to determine the mass loss behaviors of the marble samples against temperature change. The results of DTA and TGA studies are presented in Figure 4.

As a result of these studies, it was found that there was a slight weight loss of mass due to very little organic matter in the samples 2 and 4. This is also determined by the presence of trace amounts of graphite in the mineralogical analyzes in the sample 4. This situation may cause negativity in the ceramic and glass industry demanding high temperatures. On the other hand, there will be no significant impact on the other usage areas.

Surface Morphology Studies (SEM)

SEM analyses were performed in terms of raw rock and the situation that might occur as a result of grinding in terms of surface morphology characteristics. The results of the SEM study are given in Figure 5.

Figure 5 analysed shows that the calcite crystal structure in rock form is similar for 4 samples, but some changes are observed as a result of grinding. As a result of the analysis, it was found that the sample 1 came to a more homogeneous thinness and brittle. It has been found that the sample 4 is ground as crusted and leafy crumb. The fact that the sample 3 is more heterogeneous compared to the other samples seems to be negative in terms of usage areas. The sample 2 was found to be more spherical of grinding. This makes micronized calcite more advantageous in terms of its (sample 2) use than the others.

Determination of Rheological Properties (Viscometer)

The viscosity values of the ground marble wastes in the suspension are important. Brookfield Rheometer was used

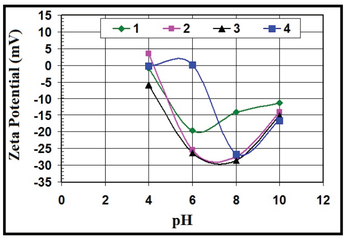

Fig. 6. Zeta potential-pH profile of the marble wastes used in the experiments
Rys. 6. Potencjał Zeta vs pH odpadów marmurowych użytych w doświadczeniach

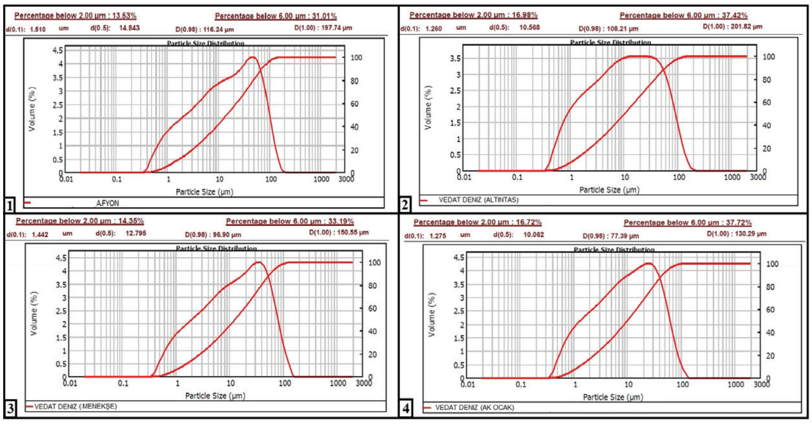

Fig. 7. Analysis of particle size distribution of the marble wastes used in experiments
Rys. 7. Analiza rozkładu wielkości cząstek odpadów marmurowych użytych w doświadczeniach

for the rheological measurements. The viscosity measurement cell has equipment providing the water circulation. In this setup, dispersions remained at a constant temperature during the measurements (22 ± 1°C). The viscosity measurements were carried out at using spindle # 1. The ground marble wastes were slurried to approximately 60% solids. The average size (d_{50}) of the samples is about 10 microns. In this respect, the viscosity values (cP) of the samples were determined and the results are given in Table 2. Measurements were made 5 times each sample and the arithmetic mean was taken.

In terms of results, the viscosity values (cP) of a calcite sample sold in the market have almost same viscosity values of the sample 1 at different velocities of the viscometer. However, the viscosity values (cP) of the samples 2, 3 and 4 have slightly larger than calcite sample sold in the market, but do not have any effect on the dispersion in the suspension.

Contact Angle Measurement Studies

The contact angles are generally determined by techniques such as "sessile drop" or "captive bubble technique" in which a water drop or a bubble contact on a mineral surface is measured from the air or liquid phase.

In order to investigate the behavior of the marble samples at different pH levels in aqueous suspensions, surface tension was calculated by measuring the contact angles and the results are given in Table 3. As the data in Table 3, the hydrophobicity of the calcite sample increases due to the surface charge in the weak acidic suspension. The hydrophobic properties, especially at neutral pH, appear to increase in almost all samples, in this respect may cause problems in suspension.

In terms of contact angle, the sample 1 has the best hydrophilic property and it has an important advantage in the use of aqueous suspensions. The sample 1 will be dispersed more rapidly in the suspension and homogeneously suspended. In sample 2, it can be readily dispersed in the suspension, as in sample 1.

Surface Charge Measurement Studies (Zeta meter)

The indirect characterization of micronized marble suspensions by measuring zeta potential is feasible because the relationship between zeta potential and apparent viscosity is valid for a lot of solid/liquid system. The zeta potentials of micronized marbles were determined by Zetasizer Nano Z (Malvern Instruments) which uses micro- electrophoresis light scattering technology.

For each sample, 5 measurement results for different pH values were obtained as arithmetic mean.

The surface charge graph depending on pH values for each sample is given in Figure 6.

In the results of experiments, all samples have high surface charge at natural pH and all samples have hydrophilic. Thus, the facts that the samples can be wetted and dispersed easily with water when suspended are advantageous for all examples.

Zeta-potential measurements of calcite were made in a narrow pH range, pH = 6-10, because of the dissolution of calcite in acidic media. The potentials for calcite mineral are Ca^{2+}, CO_2, OH, H^+ and HCO_2. Therefore, the zeta potential of the calcite at a certain pH is zero. As shown in Figure 6, for marble waste samples, the point (z.p.c.) where the charge was zero for samples 1 and 3 could be determined, whereas

Tab. 5. Viscosity values (cP) for different speed of the suspensions of marble wastes used in the experiments
Tab. 5. Wartości lepkości (cP) dla różnej prędkości zawiesin odpadów marmurowych użytych w eksperymencie

Sample	RY Whiteness	R457 Brightness	YI Yellowness
Afyon (**1**)	91.03	88.39	3.87
Altintas (**2**)	90.47	87.45	4.46
Menekse (**3**)	84.85	80.97	6.22
Ak Ocak (**4**)	88.53	85.39	4.67

the zero point charges (z.p.c.) for samples 2 and 4 were not determined.

The Tests of the Bond Grindability and the Bond Work Index (G_{bg} and W_i)

In the design of grinding circuits, the Bond grindability method is widely used for a particular material in dimensioning mills, power needs and the evaluation of performance. Its use as an industrial standard is very common provides satisfactory result in the all industrial applications. Despite having many advantages, this method has some drawbacks such as being tiring and requiring long test time also it needs a special mill [7].

The standard Bond grindability test is a closed-cycle dry grinding and screening process, which is carried out until steady state condition is obtained. This test was described as follow [8–12].

The material is packed to 700 cc volume using a vibrating table. This is the volumetric weight of the material to be used for grinding tests. For the first grinding cycle, the mill is started with an arbitrarily chosen number of mill revolutions. At the end of each grinding cycle, the entire product is discharged from the mill and is screened on a test sieve (P_i). Standard choice for P_i is 106 microns. The oversize fraction is returned to the mill for the second run together with fresh feed to make up the original weight corresponding to 700 cc. The weight of product per unit of mill revolution, called the ore grindability of the cycle, is then calculated and used to estimate the number of revolutions required for the second run to be equivalent to a circulating load of 250%. The process is continued until a constant value of the grindability is achieved, which is the equilibrium condition. This equilibrium condition may be reached in 6 to 12 grinding cycles. After reaching equilibrium, the grindabilities for the last three cycles are averaged. The average value is taken as the standard Bond grindability (G_{bg}).

The products of the total final three cycles are combined to form the equilibrium rest product. Sieve analysis is carried out on the material and the results are plotted, to find the 80% passing size of the product (P_i). The Bond work index values (W_i) are calculated from equation below.

$$W_i = 1.1 * \frac{44.5}{P_i^{0.23} * G_{bg}^{0.82} * \left[\left(10/\sqrt{P_{80}}\right) - \left(10/\sqrt{F_{80}}\right)\right]} \quad (1)$$

W_i: work index, (kwh/t)
P_i: screen size at which the test is performed (106 μm)
G_{bg}: Bond's standard ball mill grindability, net weight of ball mill product passing sieve size P_i produced per mill revolution, (g/rev)
P_{80}: sieve opening which 80% of the product passes, (μm)
F_{80}: sieve opening which 80% of the feed passes, (μm)

G_{bg} and W_i values for each marble wastes are given in Table 4.

When Table 4 is examined, it is found that the easiest grindability is the sample 2 and the most difficult grindability is the sample 3. These results have also been demonstrated in mineralogical analysis.

Micronized Grinding Tests in a Laboratory Scale Ball Mill

Micronized grinding tests of the marble wastes in a laboratory scale ball mill (0.20x0.20 m) at the same grinding conditions were performed. According to the results of the economic milling analysis, the obtained part size distribution graphs were determined by Malvern dimension analyzer and the results were given in Figure 7.

Figure 7 shows the differences in the particle size distribution of the samples milled under the same conditions. Samples 2 and 4 are the most advantageous in terms of energy cost in the grinding process because they are the largest in terms of quantities below 2 microns (16.98% and 16.72%, respectively). The sample 1 is the most disadvantageous in the grinding process because it is at least with 13.53% in terms of material content below 2 microns. The average particle size (d_{50}) of the ground samples was found to be about 10 microns in the samples 2 and 4. Therefore, it is apparent that the samples 2 and 4 will be easier to grind compared to the other the samples 1 and 3.

Determination of Optical Properties of Ground Samples by Grinding (RY, R457 and YI)

Calcite is capable of producing high quality concentrates with 98% $CaCO_3$ grade or more, which conforms to most stringent market specifications for the chemical and oil industries. However, such highly pure calcite might not satisfy the product specifications especially for filler industries concerning the brightness, whiteness and yellowness indexes. Market price of calcite powder depends on its purity: market price of purest calcite powder may be as high as there to five times that paid for toothpaste, chewing gum, paint and paper sectors. Calcite powder for paint production can be can be separated by three elements according to the optical properties. These are whiteness (RY), brightness (R457) and yellowness indices (YI). On the market, for micronized calcite with d_{50} of 2 microns, RY and R457 values should be above 90 and 85, respectively, and YI values are desired to be below 4.

The optical properties of ground marble samples were determined by Elrepho Spectrophotometer. Colour analysis studies were carried out on average particle size d_{50}: 10–15 microns. Each test was repeated three times and the values given in Table 5 are the average of three measurements.

When d_{50} = 2 microns, R457 and RY values will increase by 3–4 points and YI values will decrease by 2–3 points. From this point of view, it is seen that the samples 1 and 2 will easily overcome the optical properties demanded by the market. It is determined that the sample 4 is within the acceptance limits of market and the sample 3 is difficult to carry the standards in terms of optical properties. However, when the white parts of the sample 3 were separated with the optic sorting devices, it was concluded that the desired values would be obtained.

Conclusions

In terms of the general evaluation of many analysis performed on four different marble wastes; it is concluded that Afyon (1) and Altintas (2) samples can be used in many sectors in terms of calcite. It was determined that it was not possible to evaluate the Menekse (3) sample as calcite. On the other hand, it can be seen that Ak Ocak (4) sample can be used in some applications by further studies.

Great colour heterogeneity (grey to white variations) was observed in the Menekse (3) sample so the optical sorting was must made as a separation process to obtain high whiteness grades.

As a result of this study, it has been revealed that the properties required by the market should be investigated first in order to evaluate any marble waste as calcite.

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Ocena potencjalu pozyskania zmikronizowanego kalcytu z odpadów z białego marmuru

Naturalne węglany wapnia mają ogromne znaczenie w światowej gospodarce ze względu na ich liczne zastosowania, takie jak węglan wapnia w przemyśle papierniczym i malarskim. Produkty handlowe kalcytu muszą spełniać rygorystyczne wymagania jakościowe, które obecnie są trudne do osiągnięcia przez lokalnych producentów w Turcji. Dlatego duże ilości odpadów z przeróbki białego marmuru zostały przetransportowane do zakładów przemysłowych które wykorzystują kalcyt. Odpady marmurowe, znajdujące się w regionach Afyon i Kutahya, w środkowo-zachodniej Turcji, są ogólnie wykorzystywane do betonu i budowy autostrad. Możliwość wykorzystania odpadów marmurowych jest bardzo ważna dla rozwoju gospodarczego każdego kraju lub regionu. W artykule przedstawiono nową metodę oceny odpadów marmurowych jako krajowych zasobów kalcytu. Metoda służy jako przewodnik dla inwestorów i do podejmowania decyzji w branży kalcytu w Turcji. W artykule przedstawiono prace badawcze prowadzone w celu określenia jakości produktu - zmikronizowanego kalcytu z odpadów marmurowych oraz przegląd sytuacji rynkowej producentów regionalnych. Celem artykułu jest scharakteryzowanie czterech różnych odpadów marmurowych i określenie potencjału produkcji kalcytu o wymaganej jakości w Turcji. Zaproponowano kontrolę jakości produktów poprzez testy aplikacyjne, w tym pomiary niektórych parametrów.

Słowa kluczowe: *kalcyt, odpady marmuru, kalcyt mikronizowany, właściwości fizyczne, chemiczne, fizykochemiczne i mineralogiczne mikronizowanego kalcytu*