Micronized Calcite Potential, Production, and Principal Characteristics of Nigde (Turkey)

Emin Çiftçi and İsmail Erdağ

Abstract Marble, which is exploited for micronized calcite production in Nigde area (South Central Turkey), occurs in the Upper Cretaceous Gümüşler, Aşıgediği, and Kaleboynu Formations of the Nigde Massif. Although there are a few marble producing quarries in the area, it is long been known that the marbles of this area are generally highly fractured and don't yield large blocks or suitable slabs meeting the industrial demands. Thus, most of the production is currently carried out mainly as building stone, crushed stone, and micronized calcite. Due mainly to its high demand, micronized calcite has become a significant export product for the state's economy. Because the Nigde marbles are coarse grained with high $CaCO_3$ content, high purity, and whiteness, they are considered to be the highest quality micronized calcite quarries in the country. Consequently, the area drew many national and international investors resulting in significant increase in the number and extent of micronized calcite plants in the area. In the early 1980s, the city of Nigde had only one or two plants, it is now well over five including foreign investors and joint ventures. Annual production is also considerably increased from 20,000 to 30,000 t to almost half a million tons and it is still in increasing trend.

Keywords Micronized calcium carbonate • Calcite • Marble • Gümüşler Formation • Nigde Massif • Turkey

1 Introduction

Turkey is one of the countries with significant marble reserves in the world. Economically most important marble reserves are in the cities of the western and central Anatolia. Travertine and onyx deposits are also significant in state's economy and found in various parts of western and central Anatolia. Among these

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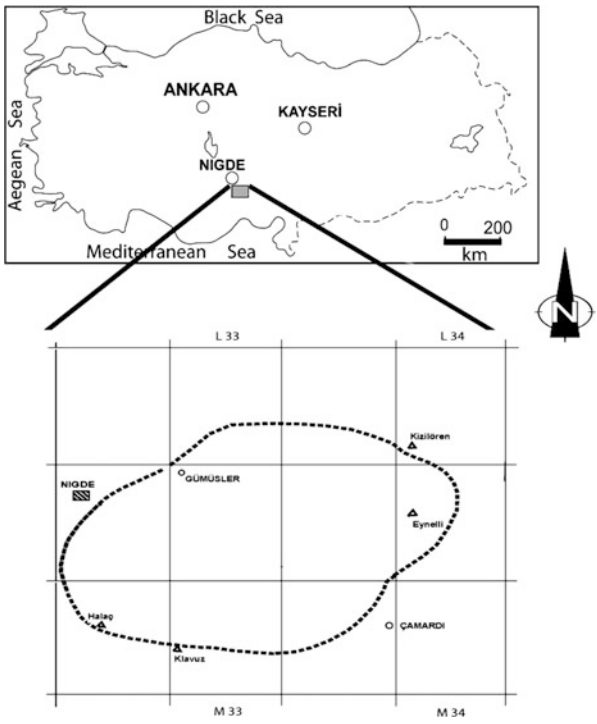

Fig. 1 Occurrences of the Nigde-white marbles in the region

places, the Nigde region (Fig. 1) prevails in terms of the reserves for high purity (low iron oxide and silica) calcium carbonate deposits.

Micronized calcium carbonate (down to 0.1 μm) production has been increasing due to the high demand from a wide variety of industrial applications, as well being an environment-friendly mineral. It has been consumed as mineral additive to soils and as acid neutralizing agent to treat wastewater and polluted lakes in many countries. Micronized calcium carbonate is also used as a filler and/or pigment by paint, paper, plastics, and ink industries. It is often used as a cheap alternative filler and pigment to replace more expensive products like titanium-dioxide, zinc oxide, and barium sulfate. According to the official records (data acquired thru personal request from the State Planning Organization), micronized calcium carbonate production increased almost fivefold during the 2004–2008 period (from about 3 million tones to over 13 million tons). Although there was a small downturn in production in 2005, the production is still showing an increasing trend [1]. More than half of this production is supplied from the city of Nigde.

Production of micronized calcium carbonate is a good approach to use calcareous rocks that are otherwise not suitable for classical applications such as slab and block marble. The major steps in production of micron-sized calcite are crushing, grinding, sizing, coating (if required), quality control, and packaging. Major industries that use micronized calcium carbonate are ink, paint, paper, plastics, construction, adhesive, leather, detergent, ceramics, food, carpet, and glass industries

Fig. 2 Field view of the Nigde-white marbles showing intense fracturing

(http://www.reade.com/es/Products/Carbonate-Compounds%2C-Powder/Calcium-Carbonate-$CaCO_3$-Powder.html; http://www.vimalmicrons.com). Coated micronized calcium carbonate is preferred for certain applications where properties such as hydrophobicity, chemical durability, high strength, and easy dispersion are needed.

The Nigde region is one of the major producers of micronized calcium carbonate. The Nigde-white marbles (as being industrial name for the marble produced in this area) crop out around the city within Gümüşler, Aşıgediği, and Kaleboynu Formations of the Nigde Massif. Most of the marbles are intensively deformed (Fig. 2); thus they are useable only as micronized calcium carbonate, dimension stone, crushed stone, and construction stone; essentially colored ones due to iron oxides staining are preferred in construction. Only a few small-scale quarries are currently operating for block production particularly from marbles of the Gümüşler Formation.

2 Regional Geological Setting

The Nigde Massif (in broad sense), representing southernmost segment of the Kırşehir Massif (or Central Anatolia Massif), which is itself a large metamorphic mass, is located in the SE of the city of Nigde, after which it is named. Southern morphology of the Massif resembles a dome with a long axis. In its north and west, it is covered and/or surrounded by Neogene tuffs (products of the Mount Hasan and Erciyes), by sediments of Mesozoic-Lower Tertiary age of Ulukışla basin in the south, and by the Ecemiş corridor (or fault zone) sediments in the east. It is first named by [2]. Blumenthal [3, 4] determined the stratigraphy and used the term "Nigde Complex," suggesting that the rocks of this massif are partially crystalline schists originated from fossil-free Paleozoic rocks. Oktay [5] prepared 1/100,000-scale geological map and made detailed petrographic determinations of the rocks. It is composed of, progressing upward, Gümüşler Formation (gneiss-amphibolite-intercalated thin marble-quartzite layers), Kaleboynu Formation (similar lithology

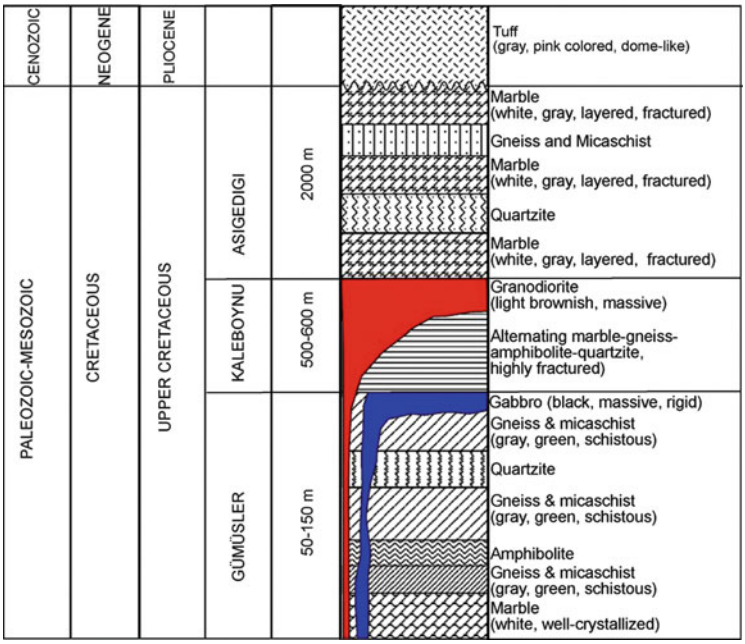

Fig. 3 Generalized geological columnar section of the study area (modified from [7, 8])

but layering is more evident), Aşıgediği Formation (white marbles—thin intercalations of amphibolite-quartzite-gneiss-calcsilicates), and Sineksizyayla Metagabbro and cut by post-metamorphism/tectonism Üçkapılı Granodiorite [6] (Fig. 3).

3 Experimental Methods

The Nigde-white marbles and micronized calcites were characterized by applying optical, physical, and chemical techniques. These include petrographic characterization of the starting materials, size distribution analyses (laser diffraction for smaller particles and sieve analyses for coarser grains), whiteness tests (using Color Eye XTH), abrasiveness (demanded by paper industry), moisture content (demanded by plastic industry), extent of coating (filler for plastic industry), scanning electron microscope analyses, chemical analyses, X-ray diffraction (XRD), percent undissolved solids in HCl, pH measurements, and oil-doped (flax oil with density of 0.98 g/cm^3) absorption values.

Table 1 Major physical parameters measured for the Nigde-white marbles [7]

Parameter	Value
Specific gravity	2.62 g/cm^3
Unit bulk weight	2.60 g/cm^3
Hardness (Moh's)	3–3.5
Water absorption by wt. and by volume under atmosphere	0.10 %, 0.25 %
Water absorption by wt. and by volume in boiling water	0.17 %, 0.27 %
Apparent porosity and porosity	0.28 %, 0.92 %
Ultrasound permeability	5,454 kg/cm^2
Compression strength	566 kg/cm^2
Percussion strength	15.6 kg/cm^2
Abrasion strength	15.9 g/cm^2
Porosity	0.92 %

Table 2 Major characteristic parameters measured for the micronized calcite produced from the Nigde-white marbles [8]

Parameter	Value	Industry requirement
Whiteness	98.68–99.64	96
Abrasiveness	8.8–11 mg/100 g	Qualified
Moisture ratio	0.15–0.28 %	Max 0.3 %
Undissolved matter ratio in HCl	0.40 %	Qualified
Mineral phases by XRD	Calcite only	Qualified
pH	9.11–9.35	Qualified
DOP absorption rate (down to 1 μm)	15–31	15–35
Oil absorption rate (down to 1 μm)	15–20	20–25
Coatability rate of coated powders (down to <2 μm)	1.22–1.48	1.50

3.1 Characteristics of Nigde Marble

Petrographic investigations of the selected samples representing the Nigde-white marble indicated that calcite occurs as chiefly equidimensional large euhedral to subhedral crystals and showed emphasized relief pleocroizm. No intergranular spaces were observed. Crystals clamped together perfectly presenting well-developed mosaic texture. Indications of tectonic deformation are clearly observed in the form of polysynthetic twinnings, calcite bucklings, and cracks. The physical parameters of the Nigde marble are listed in Table 1 [7]. Average test results for the micronized calcite samples are summarized in Tables 2 and 3 [8].

Most striking features of micronized calcium carbonates produced from the Nigde marble are their high $CaCO_3$ content up to (wt. 99 %), lower iron and silica content, and whiteness. Higher whiteness is particularly required by the dye and plastics industries in order to consume lesser TiO_2 and in paper industry to use less

Table 3 Chemical composition of selected samples for the major oxides (in wt. %) [8]

Test sample	CaO%	MgO%	Fe_2O_3%	SiO_2%	Al_2O_3%	CO_2%
UF[a] (%90 <2 μm)	53.9	0.5	<0.05	<0.05	0.15	43.8
95 (%80 <2 μm)	53.95	0.6	<0.05	<0.05	0.15	43.2
1 (%50 <2 μm)	54.4	0.55	<0.05	<0.05	0.1	43.4
2 (%40 <2 μm)	54.85	0.6	<0.05	<0.05	0.05	43.2

[a]*UF* Ultrafine

Table 4 Major micronized calcite producers in the Nigde area (Turkey)

Manufacturer	Capacity (tpy)	Product name family	PVC profile grade	Coated products	Mine ownership and operation	Distance to loading port
Esen Mikronize	70,000	Esen A	E400	Yes	Yes	20 km
Erciyes Mikronize	50,000	Ermikal	Sf1c	Yes	No	450 km
			Sf2c			
Komsar (Former Hisar)	100,000	Normcal Hydrocal	St99	Yes	No	400 km
Turmet	30,000	Turmet	None	No	Yes	350 km
Mikron'S	110,000	Turkcarb	Sm1c	Yes	Yes	350 km
Mikro Kalsit	50,000	Mikrocarb	None	No	Yes	10 km
Nigtas Mikronize	55,000	Nigkal	None	No	Yes	350 km

optical whitening. Table 4 lists major companies in the micronized calcium carbonate business in Turkey.

4 Conclusions

Subject area is located within the boundaries of Nigde, a south-central Anatolian city. High-quality micronized calcium carbonate is produced from coarse-grained, white marbles, known as the Nigde-white marbles that dominantly crop out in the Nigde Massif. The Nigde-white marbles occur in the Gümüşler, Aşıgediği, and Kaleboynu Formations. At present a few small-scale slab and block-yielding quarries are in operation in the Gümüşler Formation. The geomechanical experiments [7, 8] show that the Nigde-white marble is not suitable for slab/block marble production as a result of tectonic deformations taking place subsequent to their deposition. This study shows that the Nigde-white marbles are more suitable for the filler and pigment markets due mainly to their natural high purity and whiteness.

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