

# Production of high value added carbonate fillers from the treatment of white calcitic marble waste: the case of Eastern Macedonia and Thrace of Greece

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## ABSTRACT

*The quarrying activity for marbles' production is still a significant industrial sector in Greece, however resulting in large amounts of waste rocks equal to 95% of the extracted rock. The region of Eastern Macedonia and Thrace (N. Greece) constitutes the most important quarry center of the country where the problem of rejection of marble waste rock is particularly acute, but at the same time the rejected material possesses physical properties which make it suitable as raw material for the production of fillers. Several technical and economical aspects concerning the specific subject have been investigated by the scientific personnel of the Institute of Geology & Mineral Exploration (IGME) by implementing a number of research projects. In the framework of this study key information is provided concerning the utilisation of marble waste rock from six major quarry sub-areas in Eastern Macedonia as fillers. To this end, the actions completed include mapping of waste stockpiles together with estimation of tonnages, laboratory investigation of the materials' properties as well as examination of the domestic fillers market. Based on the market research it is apparent that despite the economic crisis, the Greek Ground Calcium Carbonate (GCC) fillers sector has remained fundamentally sound with a total annual capacity of 0.8 Mt which is mainly attributed to the increase in the exports of domestic fillers production. Also, apart from chalk and limestone, exploitation of marble residues has become a common practice for the production of GCC in Greece. Taking into account the abundance of waste marble rocks of Eastern Macedonia and the laboratory results concerning the chemical and mineralogical composition of the materials under examination, showing a CaCO<sub>3</sub> content higher than 98%, as well as the reflectance factor measurements which have values greater than 90%, utilisation of these materials looks a promising and challenging opportunity in both financial and environmental terms.*

**Key words:** mining waste, marble, fillers, Greece

## 1. Introduction

The necessity to manage extractive waste on one side and the opportunity to make something useful out of them on the other side are in fact part of the same objective: the sustainable management of mineral resources in order to achieve resource efficiency. This is extremely true in the case of white calcitic marbles which may be used for the production of Ground Calcium Carbonate, a high added value commodity, which is used widely especially by the chemical industry. According to DIN 55943 a **filler** is a substance consisting of particles which is virtually insoluble in the application medium and which is used to enlarge the volume, to achieve or improve technical properties and /or to influence optical characteristics [1]. Historically the addition

of a filler aimed at cheapening the manufacture of a product in which it was added. However, it was gradually recognised that the addition of such substances could enhance other properties of the final product and therefore the term functional filler was also applied. For example fillers addition contributes to the improvement of the mechanical properties, rheological properties and the weathering resistance of the final products. Moreover, fillers can improve optical properties as opacity, brightness and colour of the final products. Therefore, the main intrinsic physical characteristics of interest to producers and consumers of the fillers are: the mineralogical and chemical composition, fineness, abrasion behaviour, whiteness, refractive index, solubility, specific gravity, dispersion, oil absorption value etc.

Giant international GCC fillers producers, like Omya, Imerys and others have established factories all over the world and are continuously searching for good quality materials that are suitable to be used as feed in their mills. In this direction, the significance of unexploited marble quarry by-products has been highlighted many times at European level so far by institutes and researchers [2]. Since 1990, the Institute of Geology and Mineral Exploration (IGME) of Greece has accomplished a number of projects related to the utilisation of unexploited marble quarry waste. IGME is currently investigating the possibility for feasible co-management and commercial exploitation of the waste produced by the marble quarries of the Eastern Macedonia Region, mainly as fillers for the chemical industry addressing international markets, and in the field of construction, addressing mainly local markets. The Greek marbles are among the most famous ones in the world. For 2012 – 2013 the total annual production of marble products exceeded 1 million tn annually, while exports of the sector exceeded a total of 850 thousand tn worth over 240 million € (in 2013) and a total of 730 thousand tn worth over 212 million € (in 2012) [3]. The most important quarry center of Greece can be found in the rich in marble regions of Drama, Kavala-Thasos (Eastern Macedonia).

In the framework of the present article the domestic production of the domestic white carbonate fillers is presented. Details on the key-players of the sector, as well as the technical properties of the Greek commercial products are also included. Finally issues related to the types of raw materials used for GCC production are also discussed, including also marble quarry by-products from Eastern Macedonia and Thrace of Greece.

## **2. Methods**

The main scope of the present study was to investigate the potential of using marble rejects which have been produced from the past and current activity of marble quarries located in the Eastern Macedonia area (Falakro and Lekani Mountains), based also on market status including the current domestic production of fillers. More particularly, in order to capture the carbonate fillers production of Greece a market research was conducted. Details on the key-players of the sector, as well as the technical properties of the Greek commercial products were studied and issues related to the types of raw materials used for GCC production were also investigated.

Following up previous research, IGME is currently collecting data on the Eastern Macedonia past and current marble quarrying activity related to 126 marble quarries located in the areas of the Falakro and Lekani Mountains. According to estimations performed by the authors, a volume of 6.000.000m<sup>3</sup> of rocks has already been extracted so far here, but only 450.000m<sup>3</sup> were exploited for decorative purposes. The rest equal to 5.550.000m<sup>3</sup> or 15.000.000 tons have been stockpiled. An average quantity of 300.000m<sup>3</sup> (700.000 tons) rejects is currently being stockpiled annually, coming from only 11 quarries which are still operating today. The research is implemented in the framework of the National Strategic Reference Framework (NSRF) 2007-2013. It is focussing on the management and the commercial exploitation of the mining waste as fillers for the chemical industry addressing international markets, and in the field of construction, addressing mainly local markets.

The research procedure applied comprised the following activities:

- (1) Hand samples' collection of 3-5 kg weight each, correspondent to the materials rejected in the different quarrying sites of six major sub-areas in Eastern Macedonia Thrace: 1. Disvato, 2. Stenopos, 3. Komnina, 4. Limnia, 5. E. Falakro, 6. Kechrokambos. The samples were submitted in laboratory test work aimed to assess the  $\text{CaCO}_3$  content (based on XRF measurements, mineralogical examinations and chemical analysis), abrasion behaviour with an Einlehner Abrasion Tester and whiteness by measuring the reflectance factor R,% with a spectrophotometer.
- (2) Targeted bulk sampling by collecting samples of 500kg each, representing the six sub-areas mentioned above. These samples were subjected in the following treatment (**Figures 1 and 2**):
- Washing (removal of mud, fines);
  - Mechanical / physical, as well as thermal / weathering tests in accordance with: a) EN 1097.02:2011 (Methods for the determination of resistance to fragmentation - Los Angeles test); b) EN 1097.06:2000 (Determination of particle density and water absorption); c) EN 1367.02:1999 (Magnesium sulfate test).
  - Crushing – grinding and sieving tests
  - Abrasion tests with the Einlhner Anrasion Tester
  - Whiteness measurements
  - Assaying and mineralogical study
- (3) Mapping of stockpiles and GIS compilation of digital maps.



Figure 1: Bulk sample (Komnina)

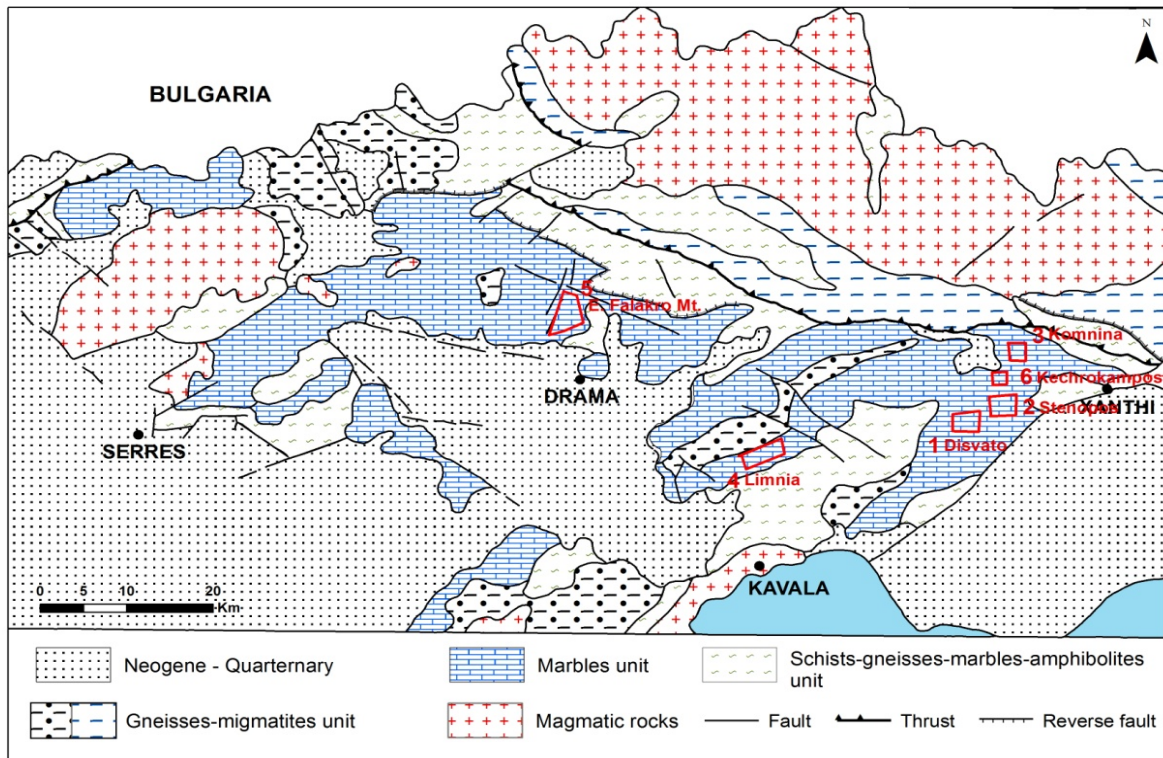


Figure 2: Laboratory treatment of bulk samples

It should be noted here that the geological study of the area under investigation is of extreme importance for the following reasons:

- Access to stockpiles of marble waste is often difficult and collection of representative samples is not possible;
- Study of the qualitative characteristics of the marble waste material is based on hand samples typical of the rock formations that occur in the area;
- Exploitation of rejects for specific applications depends on: a) the availability of materials that own the necessary specifications, and b) the possibility to select and remove the desirable qualities;
- Correlation between qualities and quantities must be accomplished with the help of an expert geologist in co-operation of course with a mineralogist;
- Further proposals for management and exploitation of the marble waste should be based on the results of such investigation.

**Figure 3** depicts the geology of the area and the position of each sampling area [4].



**Figure 3:** The six sampling areas of marbles rejects located in the Eastern Macedonia

### 3. Results and Discussion

#### 3.1 Major applications of GCC fillers

Fillers are used in various applications with the two most important being the processing of plastics and elastomers. Other applications in descending order are: papermaking sector, paints and varnishes industry, and adhesives and sealants industry [5]. The filler content in the final product depends on the application to be used. For example, the elastomer industry uses filler content of 50-60% for tyres production, 40 – 60% for the manufacturing of floor covering, 35 – 55% for roofing sheets production, 5 – 15% for shoe soles manufacturing and 60 – 80% for carpet backing while the thermoplastics industry uses filler content of 20-30% for the production of indoor applications, 20-40% for the production of PP garden furniture, 3 – 30% for PVC pipe production and 2-30% for PE film and sheet production [6]. Moreover, in the paper industry for the production of newsprint the filler loading is up to 12% while for the manufacture of Supercalendered (SC) papers the loading levels amount to 35% [7]. Finally, in the coating industry 50-70% of filler loading is used for the production of emulsion paints, 70-80% in the synthetic resin bound plasters and stoppers, 30 – 40% in the road-marking paints and 10 – 20% in powder coatings [6].

Based on *Ceresana (2014)*, globally, the most commonly used fillers are Ground Calcium Carbonate (GCC), followed by Precipitated Calcium Carbonate (PCC) and carbon black. Moreover, kaolin and talcum are also used in significant quantities. All other types of fillers reached an aggregated market share of only 9% [5]. Given that fillers can be used in manifold applications in various industrial sectors, it is expected that the sales markets for fillers will develop very rapidly. It is worth mentioning that *Ceresana (2014)* foresees that the global market for fillers to generate revenues of approximately US\$27.7 billion in 2021 [5].



### 3.2 Key players for the production of GCC in Greece

In Greece, the main companies involved in the production of carbonate fillers are the DIONYSSOMARBLE, the IONIAN KALK SA, the MICROFILL SA, the KARBOKAL SA and the OMYA HELLAS SA. Furthermore, WHITE MINERALS SA is the Greek huntine producing company, while the INDUSTRIAL MINERALS SA produces and sells semi-processed intermediate products, using marble GCC raw materials [8]. In **Figure 4** the geographical distribution of the Greek companies which produce GCC are presented.



**Figure 4:** The geographical distribution of the Greek companies which produce GCC

In particular, since 1975 the **DIONYSSOMARBLE** has been producing crystalline calcium carbonate powder filler in controlled granular sizes under the trade name "NOVOCARB". The raw material for the production of fillers is mainly marble waste rocks produced during marble extraction from the Dionyssos - Pentelicon quarry located

in Attica. The production unit is located close to the quarry. In the filler plant, the manufacturing process involves raw meal grinding, air jet separation, and when ordered stearic coating which is a wax extracted from trees in Southeast Asia (trade name of products: NOVOCARB COATED). The CaCO<sub>3</sub> powder is produced in various grain distributions using air jet separation, depending on the demands of the clients. In **Table 1** the major properties as well as applications of the fillers produced by DIONYSSOMARBLE are presented. The typical chemical analysis of the products is: CaCO<sub>3</sub> 98 %, 0.35% SiO<sub>2</sub>, 0.75% MgO, 0.07% Fe<sub>2</sub>O<sub>3</sub> and 0.01% Mn<sub>2</sub>O<sub>3</sub> [9, 10].

**Table 1:** Properties and applications of the Marble GCC products produced by DIONYSSOMARBLE

Trade name: NOVOCARB	Fineness			Y*	Applications
	d <sub>0,97</sub> µm	d <sub>0,50</sub> µm	%<2		
<i>Uncoated</i>					
No 10	8 - 12	3 - 5	25 - 35	98.0	Paints, Plastics and Adhesives
No 20	16 - 20	4 - 6	14 - 26	97.5	Paints, PVC, Adhesives, Stucco with polyester base
No 25	23 - 27	5 - 8	12 - 18	97.0	Paints, PVC, Adhesives, Stucco with polyester base
No 40	38 - 42	11 - 14	7 - 10	97.0	Paints, Plastics, Carpets, Tyres, Insecticides, Pesticides
No 60	58 - 62	12 - 18	5 - 8	96.5	Acrylic stucco, Carpets, Detergents, Insecticides, Pesticides, Tyres
No 80	78 - 82	21 - 24	5 - 7	96.0	Acrylic stucco, Carpets, Detergents, Insecticides, Pesticides, Fertilisers, Feeds
No 120	115 - 125	30 - 35	4 - 6	96.0	Carpets, Detergents, Insecticides, Pesticides, Fertilizers, Feeds, Tyres
SoftGrade no 100	58 - 62	12 - 18	5 - 8	96.0	Putties, Roofs covering, Films for greenhouse covers
<i>Coated</i>					
No 10c	8 - 12	3 - 5	25 - 35	98.0	Cable, PVC tube, Paints
No 20c	16 - 20	4 - 6	14 - 26	97.5	Cable, PVC tube, Paints
No 25c	23 - 27	5 - 8	12 - 18	97.0	Cable, PVC tube, Paints

Y\*: Whiteness index ASTM 313

Until 2008 more than 90% of total production is consumed domestically and covers needs of the paint and plastics (PVC, cable production) [8]. Today (2015) the picture has changed due to the economic crisis and a shift towards exports has been noted. More particularly, due to exports increase (approx. 45% of the production) the annual production of fillers has remained relatively stable in recent years.

The **IONIAN KALK SA** is engaged in mining and processing of amorphous calcium carbonate and processing of talcum for the production of fillers. The raw material is extracted from the company's own quarries of Minies on Kefalonia Island while the processing takes place at the two (2) production units of the company which are located at Minies (Kefalonia) and at Mandra (Attica). The company's products are intended for industries of paint, plastics, rubber, paper, cement, ceramic, etc. and used in the production of adhesives and sealants, blasting material, fertilizers, road construction materials, chemicals, construction materials etc. The company exports (approx. 80% of the production) to more than sixty five (65) countries such as Russia, United Arab Emirates, India, South-East Africa, North Africa, Mediterranean countries, South America, Saudi Arabia, the Balkans, North Europe etc. In **Table 3** the technical characteristics of the produced fillers of IONIAN KALK SA are given. The typical chemical analysis of the products is: CaCO<sub>3</sub> 99 %, 0.05% SiO<sub>2</sub>, 0.15% MgO and 0.01% Fe<sub>2</sub>O<sub>3</sub> [11].

**Table 3:** Technical characteristics and applications of the GCC products produced by IONIAN KALK SA

Trade Name: IOKAL	Top cut $d_{97} \mu\text{m}$	Median size $d_{50} \mu\text{m}$	L*	Y (%)	Abrasion Einlehner mg	Applications
<i>Uncoated</i>						
ULTRA FINE	3.5 ( $d_{98}$ )	0.75	98.5	$\geq 96.0$	2.3	Paints: <i>Emulsion paints, alkyd paints</i> Paper: <i>Coated paper, wallpaper</i> Plastics: <i>PVC extrusion rigid &amp; plasticized, injection moulding, calendered sheets, coatings</i> Rubber, Adhesives
SPECIAL CHALK	17.5	2.3	96.5	$\geq 92.0$	8.0	School chalks
TYP 5C	7	1.9	98.5	$\geq 95.5$	4.2	Paints: <i>Emulsion paints, alkyd paints</i> Plastics: <i>Rigid &amp; Plasticized PVC, Injection moulding, Calendered sheets, Coatings</i> Paper: <i>Coated paper, Wallpaper</i> Rubber, Adhesives
TYP 10C	10.0	2.4	98.0	$\geq 95.5$	5.6	Paints: <i>Interior and Exterior emulsion paints, Alkyd paints</i> Plastics: <i>PVC, PPP</i> Paper, Rubber, Chewing gums
No 20	20.0	3.7	98.0	$\geq 94.5$	11.4	Paints: <i>Interior and exterior emulsion paints, oil and synthetic resin systems</i> Plastics: <i>PVC coatings</i> Adhesives
No 40	30.0	4.5	98.0	$\geq 94.0$	14.5	Paints: <i>Interior and exterior emulsion paints, Oil &amp; resin systems, putties</i> Plastics: <i>PVC</i> Rubbers, Adhesives, Polishes
KALKOLIN	32.0	6.0	96.0	$\geq 90.0$	11.0	Paints: <i>Interior and exterior emulsion paints</i> Plastics: <i>PVC pipes</i> Adhesives, Polishes (Lacquers)
No 63	48.0	6.5	97.0	$\geq 93.0$	21.1	Paints: <i>Polymer based plasters, latex coatings</i> Carpets, Adhesives
TYP RL	50.0	7.0	97.5	$\geq 93.5$	26.4	Paints: <i>Exterior paints, Latex coatings, Polymer based plasters</i> Adhesives
No100	63.0	-	96.5	$\geq 93.0$	19.0	Paints: <i>Exterior paints, mat paints</i> Plastics: <i>PVC, latex coatings and</i> Carpets, Adhesives, Polishes
<i>Coated</i>						
ULTRA FINE	3.5 ( $d_{98}$ )	0.75	98.5	$\geq 96.0$	2.3	Plastics: <i>PVC extrusion plasticized, PVC injection moulding, calendered sheets, PVC Coatings, PVC profil</i> Rubber, Sealing compounds
TYP 5C	7	1.9	98.5	$\geq 95.5$	4.2	Plastics: <i>PVC extrusion plasticized, PVC injection moulding, calendered sheets, PVC Coatings, PVC profil</i> Rubber, Sealing compounds
TYP 10C	10.0	2.4	98.0	$\geq 95.5$	5.6	Plastics: <i>Cable compounds, Coatings, Calendered sheets, PVC profil, PVC pipes, Injection moulding compounds, PE masterbatch</i> Rubbers
TYP 15C	13.5	2.9	98.0	$\geq 95.0$	8.3	Plastics: <i>Plasticized PVC extrusions, PVC foam, PVC coatings</i> Paints: <i>Primers</i> Rubber, Adhesives, Sealing compounds
IOKALIT A	10.0	3.7	97.5	$\geq 94.0$	6.5	Paints: <i>Oil paints, Alkyd paints, Anticorrosive paints, Primers, Industrial finishes</i> Plastics: <i>PVC, PE, PPP</i>
KALKOLIN	23	4.5	96.0	$\geq 90.0$	11	Plastics: <i>PVC pipes</i>

The **MICROFILL SA** produces fillers from calcium carbonate and talc. The raw material is limestone and imported talc. The company holds a leading market share in Greece that complements its genuine export orientation. Nowadays, 80% of its output is exported. The company has been a reputable supplier to numerous industrial users operating in the international paints and plastics markets. Core applications refer to construction paints, PVC compounders for cables, window profiles, and pipes, as well as PPE and PE masterbatch producers. The chemical analysis of the calcite products is: 99.5% CaCO<sub>3</sub>, 0.32% MgO, 0.040% SiO<sub>2</sub>, 0.010% Fe<sub>2</sub>O<sub>3</sub> and 0.003%Al<sub>2</sub>O<sub>3</sub> while for the talcum products the typical chemical composition SiO<sub>2</sub>: 62 - 63 %, MgO : 30 - 31%, CaO : 0.40%, Fe<sub>2</sub>O<sub>3</sub> : 0.15% and Al<sub>2</sub>O<sub>3</sub>: 0.32% [12].

**Table 4:** Technical characteristics and applications of the fillers produced by MICROFILL SA

Raw Material	Trade Name	Median size d <sub>50</sub> μm	Top cut d <sub>97</sub> μm	Whitness L*	Main Applications
<i>Uncoated CaCO<sub>3</sub> grades – MICROBLANC</i>					
Very white Calcite of highest purity	X-treme	1.0	5	98.0	Paints as TiO <sub>2</sub> extender, jnpaper
	1	1.6	7.5	97.5	Paints, PO/PE masterbatch
	2	2.0	10	97.0	Paints, Paper, Food
	3	3.5	15	96.5	Paints, Sealants
	5	4.5	22	96.5	Paints, Sealants, Adhesives, Food
	130	85	300	93.0	Paints, Adhesives, Putties
	20	11	85	93.0	Adhesives, Putties, Glass, Rubber
	Matting	24	55	95.5	Emulsion paints as matting agent
<i>Double Coated CaCO<sub>3</sub> grades – ZETAFIL</i>					
Very white Calcite coated by Stearic acid	cst 1	1.1	3.5	98.0	PVC window profiles
	cst CA	1.7	6.5	97.5	PVC profiles, pipes, cables, PO MB
	cst 2	3.0	10	97.0	Masterbatch, PVC pipes, cables
	cst 3	3.5	14	97.0	Masterbatch, PVC pipes, cables
	MST	5.5	22	96.5	PVC pipes, Solvent based paints
<i>Talcum grades – ZETATALC</i>					
Extremely white macrocrystalline Talcum	EW 10	4.0	13	97.0	Paints, PO/PE masterbatch
	EW 20	6.0	22	96.5	Paints, PO/PE masterbatch
	EW 40	16	60	95.0	Paints, Cables

Apart from the abovementioned companies, KARMPOKAL SA and OMYA HELLAS SA are also producing fillers through the valorisation of marbles by-products from North Greece.

Based on the collected primary data, today (2015) the total annual capacity of Greek enterprises producing fillers remained at the same level as that of 2008, i.e. about 0,8Mt. Relatively stable to slightly increasing trends is the annual domestic production of fillers (2015) which ranges from 0.3 to 0.5 Mt. Despite the fact that the economic crisis negatively affected the Greek industry, domestic production of fillers showed a slightly upward trend in prices before the crisis (2008). This can be attributed both to the importance of these materials for use in specific industries (plastics, paints) at national level and to the fact that the sector is strongly export oriented. Specifically, it is estimated that over 80% of the production volume is exported. Regarding the prices of these carbonate products, they are ranging from 35 to 320 € / t, depending on the raw material and processing that they undergo. As for the domestic use, it is mainly absorbed by the paint industry and plastics, since the domestic paper industry uses little mineral fillers in the production of primary and produces pulp. With regard to the global consumption of calcium carbonate (filler grade) in 2011 amounted to 74Mt, of which 60Mt was GCC and 14Mt was PCC [13]. In 2011, globally, the paper industry (39%) followed by the plastics



industry (26%) constituted the largest markets for both GCC and PCC products. Asia is the largest consumer of these products and is responsible for consuming almost half the global production volume of GCC and PCC for 2011 [13]. The global market for calcium carbonate is expected to reach 98.7 Mt by 2020 mainly due to requirements in paper and plastic production [13]. According to *Roskill (2012)*, overall, the current market trends related to calcium carbonate are: (a) the replacement of the kaolin with calcium carbonate in the paper industry, (b) the requirement for products with a grain size at the nano polymer industry, (c) the use of calcium carbonate in the pharmaceutical industry, (d) the growing interest in the use of a larger load of calcium carbonate in the paper industry and (e) the increasing consumption of calcium carbonate from the paint industry [13].

### 3.3 The potential of marble waste from the Eastern Macedonia for the production of GCC

Key properties of marble rejects from the area under study, regarding their application in the calcium carbonate fillers industry are summarised in **Tables 5a, 5b** and **Table 6** below. The results are based on examinations performed at IGME's laboratories on hand samples and bulk samples collected during the years 2013 and 2014 (see **Figure 5**).

**Table 5a:** Optical properties and CaCO<sub>3</sub> content of the materials in the area under study, based on hand samples

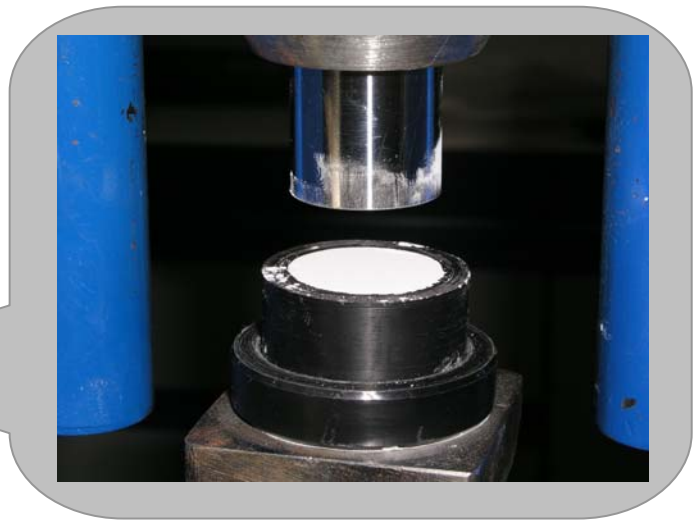
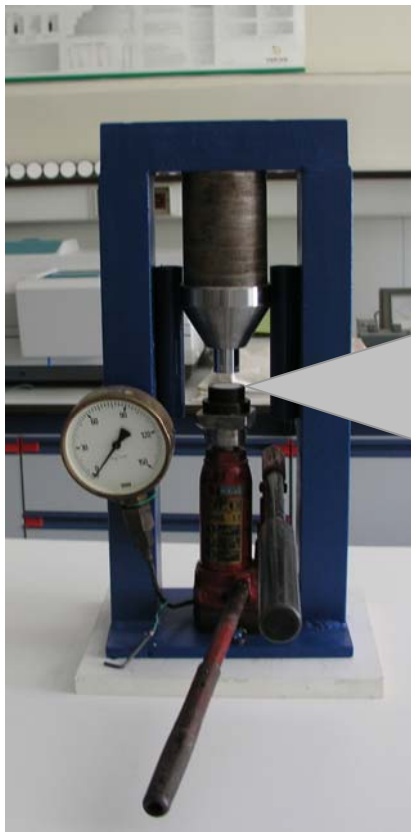
Sub- area of interest	Abrasive <sup>(a)</sup>		Optical Properties <sup>(b)</sup>				Purity
	Einlehner mg	VWB <sub>120</sub>	L* (%)	a*	b*	Tristimulus value Y (%)	CaCO <sub>3</sub> , %
1. Disvato	20.2-28.1 (24.6)	66.2-92.1 (80.7)	96.9-97.8	-0.092 to -0.046	0.042 to 0.114	92.2 - 94.5	99
2. Stenopos (white)	26.3-29.6 (27.9)	86.2-97.0 (91.5)	97.6-98.2	0.001 to 0.052	-0.027 to 0.592	93.9 - 95.6	98-99
3. Komnina (white)	24.6-28.2 (26.6)	80.7-92.5 (87,2)	98.3-98.4	0.020	0.564 to 0.695	95.7 - 95.9	99
4. Limnia (white and semi-white varieties)	23.5-29.0 (25,7)	77.0-95.1 (84.3)	96.8-98.1	-0.098 to 0.088	-0.229 to 0.632	90.0 - 95.2	99-100
5. E. Falakro (white & semi-white varieties)	25.3-28.0 (26.7)	83.0-91.8 (87.5)	96.5-98.5	-0.077 to 0.075	-0.019 to 0.0556	91.2 - 95.8	98-99
6. Kechrokambos (white)	24.7	81	98.3	0.020	0.499	95.7	98

**Table 5b:** Optical properties and CaCO<sub>3</sub> content of the materials in the area under study, based on bulk samples

Sub- area of interest	Abrasive <sup>(a)</sup>		Optical Properties <sup>(b)</sup>				Purity
	Einlehner mg	VWB <sub>120</sub>	L* (%)	a*	b*	Tristimulus value Y (%)	CaCO <sub>3</sub> , %
1. Disvato	14.6	47.9	97.4	-0.0185	0.4757	93.6	99
2. Stenopos (white)	17.5	57.4	97.4	0.0376	0.8250	93.4	98
3. Komnina (white)	18.1	59.3	98.2	0.0714	0.8780	95.4	98
4. Limnia (white and semi-white varieties)	15.9	52.1	97.3	-0.0686	0.3419	93.2	99
5. E. Falakro (white & semi-white varieties)	17 (B) 19.3 (A)	55.7 (B) 63.3 (A)	96.2 (B) 95.9 (A)	-0.1334 (B) -0.1116 (A)	0.0610 (B) 0.0235 (A)	90.5 (B) 89.8 (A)	99 (B) 99 (A)
6. Kechrokambos (white)	19.0	62.3	97.9	0.0439	0.6930	94.8	99

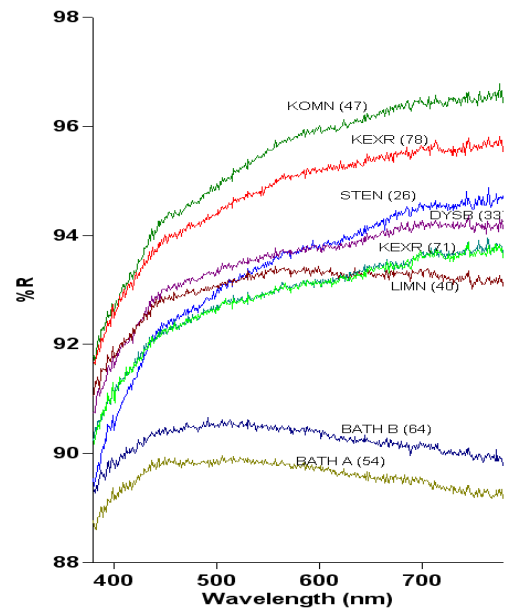
(a) Grain size  $d_{90}=30\mu\text{m}$

(b) Grain size  $d_{90}=30\mu\text{m}$ , 8° Diffuse Reflectance Spectrophotometry CIE 10° Observer, Illuminant D65, Standard: BaSO<sub>4</sub> powdered



**Figure 5:** Measurements of the reflectance values with a CARY 100 spectrophotometer. The material is pressed and then is measured compared to a similar specimen prepared from a standardised BaSO<sub>4</sub> powder. The following standards apply:

1. ASTM E 1331-04 'Standard Test Method for Reflectance Factor and Color by Spectrophotometry Using Hemispherical Geometry', παράρρ. 5.2.2.3.
2. ASTM E 1164-09a 'Standard Practice for Obtaining Spectrometric Data for Object-Color Evaluation'
3. ASTM E 313-05 "Standard Practice for Calculating Yellowness and Whiteness Indices From Instrumentally Measured Color Coordinates"
4. ASTM 308-06 'Standard Practice for Computing the Colors of Objects by Using the CIE System'



**Table 6:** Mineralogical composition of the materials in the area under study

Sub- area of interest	Mineralogical composition		
	Calcite, %	Dolomite, %	Others (mainly quartz), %
1. Disvato	96.9-97.3	2.4-2.6	0.3-0.8
2. Stenopos	96.3-96.9	2.7-3	0-0.7
3. Komnina	97-97.3	1.7-2.3	0.6-1
4. Limnia	97-98%	1.5-2.5	0-1
5. E. Falakro	95-97.5	1.3-3.1	1-1.3
6. Kechrokambos	96.5	1.5	0.7-1.8

It is obvious that these materials are of great interest to the fillers industry, since they are pure calcitic, having  $\text{CaCO}_3 > 98\%$ , with high reflectance values ( $Y = 90-96\%$ ) for the powdered material.

#### 4. Conclusions

Despite the fact that the economic crisis negatively affected the Greek industry, the GCC fillers sector has remained fundamentally sound with a total annual capacity (2015) equal to 0.8 Mt. This can be attributed to the importance of fillers for the domestic plastics and paints industries as well as to the fact that the sector is strongly export oriented. In particular, it is estimated that over 80% of the production of the domestic production of GCC fillers is exported. In Greece, the raw material used to produce GCC is basically microcrystalline limestone. However, apart from limestone, the utilization of marble residues has become a common practice for the production of GCC in Greece. Across the world, the global market of filler grade calcium carbonate was 74 Mt in 2011 and is expected to reach 98.7 Mt until 2020, including also PCC. Within this framework and given the abundance of waste marble rocks of Eastern Macedonia with excellent characteristics ( $\text{CaCO}_3 > 98\%$ ,  $Y = 90-96\%$ ), the production of high value added carbonate fillers from the treatment of white calcitic marble waste constitutes a sustainable prospect.

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