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ScienceDirect

Energy Procedia 125 (2017) 656–665

Energy Procedia

www.elsevier.com/locate/procedia

European Geosciences Union General Assembly 2017, EGU Division Energy, Resources & Environment, ERE

Characterization methodology for re-using marble slurry in industrial applications

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Abstract

Due to the widespread use of calcium carbonate as a raw material in a number of industrial fields, the recovery of marble waste and its processing in a marketable product is nowadays gaining an economical interest.
Marble slurry waste samples were chemically, physically, mineralogically and morphologically analyzed and the obtained data were compared with marketable micronized $CaCO_3$ specifications. The results have shown that marble waste could be re-used as a raw material in different industrial processes with no or light treatments.
Besides the economic benefits, transforming a waste into an important economic resource involves environmental advantages and sustainability promotion.

Peer-review under responsibility of the scientific committee of the European Geosciences Union (EGU) General Assembly 2017 – Division Energy, Resources and the Environment (ERE).

Keywords: marble waste; calcium carbonate filler; dimension stone; environmental impact.

1. Introduction

Dimension stone section has gone progressively widening, assuming a strategic role in worldwide economy.

The 2015 production was placed in the order of 82.6 million tons with a percentage of the waste extraction and processing amounting to over 70 % of the gross quantity [1]. In the European Union, the Italian pre-eminence was consolidated with over 30 % of volume. The quarry productions and the processing wastes related to the seven leading stone countries are reported in Table 1.

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1876-6102
Peer-review under responsibility of the scientific committee of the European Geosciences Union (EGU) General Assembly 2017 – Division Energy, Resources and the Environment (ERE).
10.1016/j.egypro.2017.08.277

Table 1. Quarry productions and processing wastes in the World [1].

LEADING STONE COUNTRIES	QUARRY PRODUCTION [kt]	PROCESSING WASTE [kt]
CHINA	45,000	22,768
INDIA	21,000	6,285
BRAZIL	8,200	2,990
TURKEY	10,500	2,493
ITALY	6,500	2,485
SPAIN	4,750	1,641
PORTUGAL	2,700	812

The increased production of natural stone waste as well as its impact on the environment have been the main focus of debate within the scientific community. The studies are generally focused on waste minimization, according to a circular economy perspective.

Dimension stone waste is divided in two main categories: waste deriving from quarrying activities and waste deriving from processing plants.

This research is focused on marble slurry waste, consisting in fine-grained residues resulting from operations of cutting and polishing, recovered at the end of the waste water purification system, and that could be processed to be re-used as raw materials suitable for applications in other industrial sectors [2, 3], such as building industry [4, 5].

Generally, wastes are materials which the owner or holder wishes to dispose of, and, in some cases, their collection and treatment as waste is required by the public interest [6]. The term "waste" has a negative image because it qualifies a material from the perspective of the upstream activity that generated it. However, it does not in any way mean that recovery or recycling is excluded [7, 8]. The possibility to re-use the slurry is related first of all with the compliance with the regulatory framework.

The European Union defines the situation of waste with three European directives: 2006/21/EC on the management of waste from extractive industries - 2008/98/EC on waste - 1999/31/EC on the landfill of waste [9, 10, 11].

The aim of this paper is to propose a defined way to characterize marble slurry in order to obtain useful data to make a comparison with market specifications. Further goal is to enhance the environmental advantages of re-using stone waste by reducing marble waste landfills and by applying raw material replacement, thus pursuing the objective to convert natural stone waste into by-product with a renewed environmental and economic value.

2. Materials and Methods

2.1. Materials

The materials investigated have been chosen according to the aims of the research program. Two of the numerous industrial marble processing plants have been selected with a consideration to the kind of material processed, the volume of production, the accessibility and the cooperative attitude of the owners.

The two selected processing plants are located in the Orosei marble district, in the North-Eastern Sardinia, Italy (Fig. 1), where the quarrying of a highly appreciated stone variety is an important economic activity; fifteen quarries and fifteen stone processing plants currently operate in the area [12]. Part of the quarries production is processed in different plants obtaining different kinds of final commercial products [13]. As a result, a waste material consisting of very fine particles, in the form of slurry, is also produced. The investigated marble slurry samples have been collected at the end of the filter press section of the two plants selected.

Fig. 1. Current aerial view of Orosei Marble Industrial Zone "D" (gps coordinates: 40°21'39.19"N; 9°39'48.72"E)

2.2. Methods

Before starting the analysis phase, marble slurry samples, containing about 25% moisture, were dried in oven at a temperature of 110 ± 5 °C until they reached the constant weight, then reduction by quartering was made, in order to obtain the representative samples of a convenient size for testing.

The collected materials were completely characterized by the proposed methodology, which follows four main steps: chemical - physical - mineralogical and morphological determinations.

Conventionally, the original purpose of waste characterization was to determine if a waste needs to be managed as a hazardous or inert waste, thus, analytical samples were prepared for leaching test submission. The method was made by performing the compliance leaching test EN 12457-2 [14] on the untreated marble slurries which were sampled according to the UNI 10802 procedure [15].

Sample solutions were prepared with the techniques of lithium metaborate fusion and acid digestion, for detecting major oxides and trace elements with the inductively coupled plasma atomic emission spectroscopy. According to the ASTM C25 [16], the loss on ignitions (LOI) were also calculated [17].

Then grain size distribution and specific gravity were determined, respectively, by SediGraph 5100 Analyzer and gas-pyknometer AccuPyc 1330 equipment, manufactured by Micromeritics Instruments, in accordance with EN 1097-7 [18, 19].

In some industrial applications chromatic characteristics of carbonate powder are among the market parameters required to be determined. Therefore the measurements for colorimetry and brightness characterization were carried out on all the samples taken from the filter presses. Representative samples were submitted to colorimetric and brightness analysis with the support of a spectrophotometer CM 3610-A produced by Konica Minolta, set with the white calibration plate CM-A139 and equipped with powder mould, applying the UNI 8941-1 [20].

The mineralogical characterization and the identification of the crystalline phases were performed through a Rigaku device with Cu-Ka radiation (copper tube operated at 30 kV and 30 mA) with a step size of 0.02 °2θ and scanning time of 0.6 second per step.

Scanning electron microscopy, equipped with Phenom ProX, was used to detect the morphological quality of the marble particles.

3. Results and discussion

Waste parameters were measured in the eluates, whose concentrations are below the Italian Decree No. 281, 2010 limits specified in Table 2. The analytical results confirm that these residues are classified as inert as it does not exceed the concentration limits for the acceptability in landfills for inert waste.

Table 2. Marble slurries leaching test results [mg/L].

PARAMETERS	LIMIT	FACTORY 1	FACTORY 2
Mo	0.05	< 0.007	< 0.007
Ba	2.00	< 0.0001	< 0.0001
Sb	0.006	< 0.005	< 0.005
Cu	0.05	< 0.005	< 0.005
Zn	3	< 0.005	< 0.005
Ni	0.01	< 0.005	< 0.005
As	0.05	< 0.02	< 0.02
Cd	0.005	< 0.002	< 0.002
Cr_{tot}	0.05	< 0.005	< 0.005
Pb	0.05	< 0.02	< 0.02
Se	0.01	< 0.02	< 0.02
Hg	0.001	< 0.0005	< 0.0005
pH	5.5 < > 12	9.16	9.34

Data of chemical compositions and relative proportions in oxides are indicated in Table 3, along with the LOI values and the specific gravities, calculated as average value of the different measurements carried out. All the trace elements were detected but they are not indicated because of their irrelevant concentration rate that could justify an interest for the present research.

Table 3. Marble slurries chemical characterization data.

PARAMETERS	FACTORY 1	FACTORY 2
SiO_2 [%]	0.14	0.16
Al_2O_3 [%]	0.04	0.04
$Fe_2O_{3(T)}$ [%]	0.03	0.04
MnO [%]	< 0.01	< 0.01
MgO [%]	0.42	0.51
CaO [%]	56.11	56.01
Na_2O [%]	0.01	0.01
K_2O [%]	<0.01	< 0.01
TiO_2 [%]	< 0.005	< 0.005
P_2O_5 [%]	0.02	0. 05
LOI [%]	44.00	43.70
TOTAL [%]	100.77	100.52
Specific Gravity [g/cm^3]	2.7111	2.7131

These very fine particles present chemical and nature similar to pure calcium carbonate. As a matter of fact, the analyzed marble slurries contain very minor amounts of impurities and the values, obtained for the loss on ignition, demonstrate that the samples have high content of calcium oxide, consequently it is clear that the original stones are nearly pure carbonate.

The grain size curves of representative samples are reported in Fig. 2. It is important to note that the particles are very fine, as resulted in the grain size curves, in the order of the micrometer. The main fraction, approximately 90% of the material, exhibits grain sizes of below 20 μm.

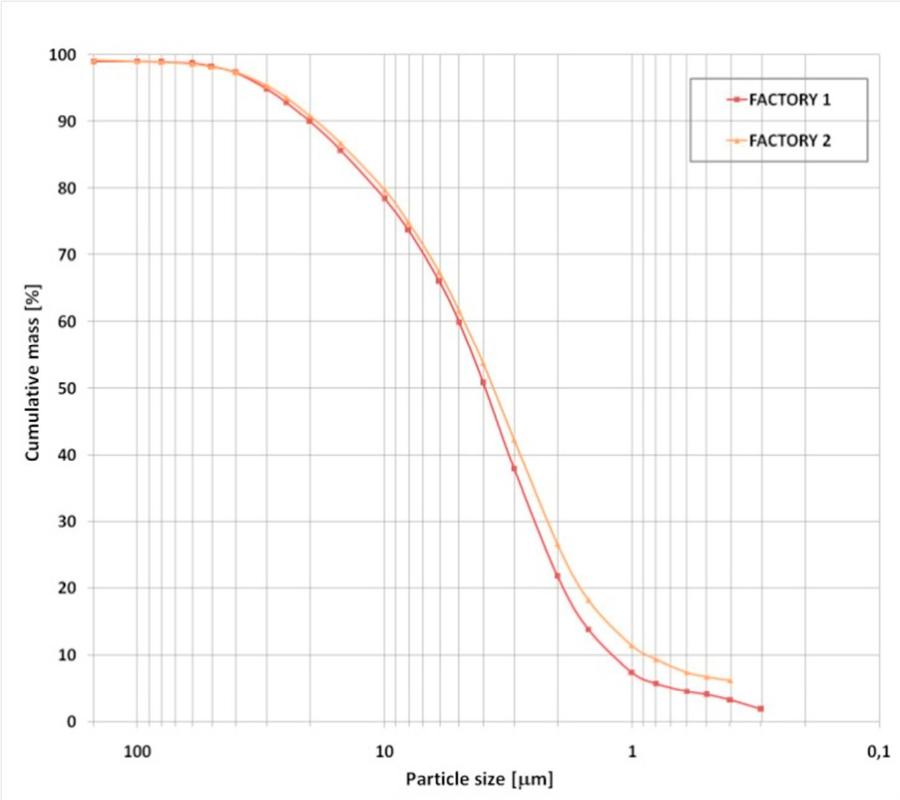

Fig. 2. Grain size curves.

Among the merchandising parameters required to calcium carbonate powder, for some application fields, there are also the chromatic characteristics. Therefore the measurements for colorimetry and brightness determination were carried out on the samples taken from the filter presses. The surveys were carried out according to what was fixed by the Standard of the Italian Unification Office.

Table 4. Marble slurries colorimetric and brightness values.

PARAMETERS	UNIT	FACTORY 1	FACTORY 2
Brightness ISO	%	81.04	85.21
L* (D65)	SCI	94.47	95.82
a* (D65)	SCI	0.65	0.47
b* (D65)	SCI	4.27	3.40

Interestingly, the powder produced by factory 2 is found to have a higher brightness than the other. On the contrary, the factory 1 powders is more opaque. This could be due to the use of the resin and the consumption of grinding wheels and polishing agents in the honing-polishing line of the company.

Data, summarized in Table 4, show a high tendency towards white for factory 2 slurry that is a strategic parameter for the paper industry.

Determinations were carried out for identifying the marble powder mineralogical composition. As demonstrated in the following figure (Fig. 3), XRD spectra of the two dewatered slurries, show that calcite is the only mineral constituent detected. Mineral phases were determined by comparison with the ICDD index, 47-1743 PDF [21].

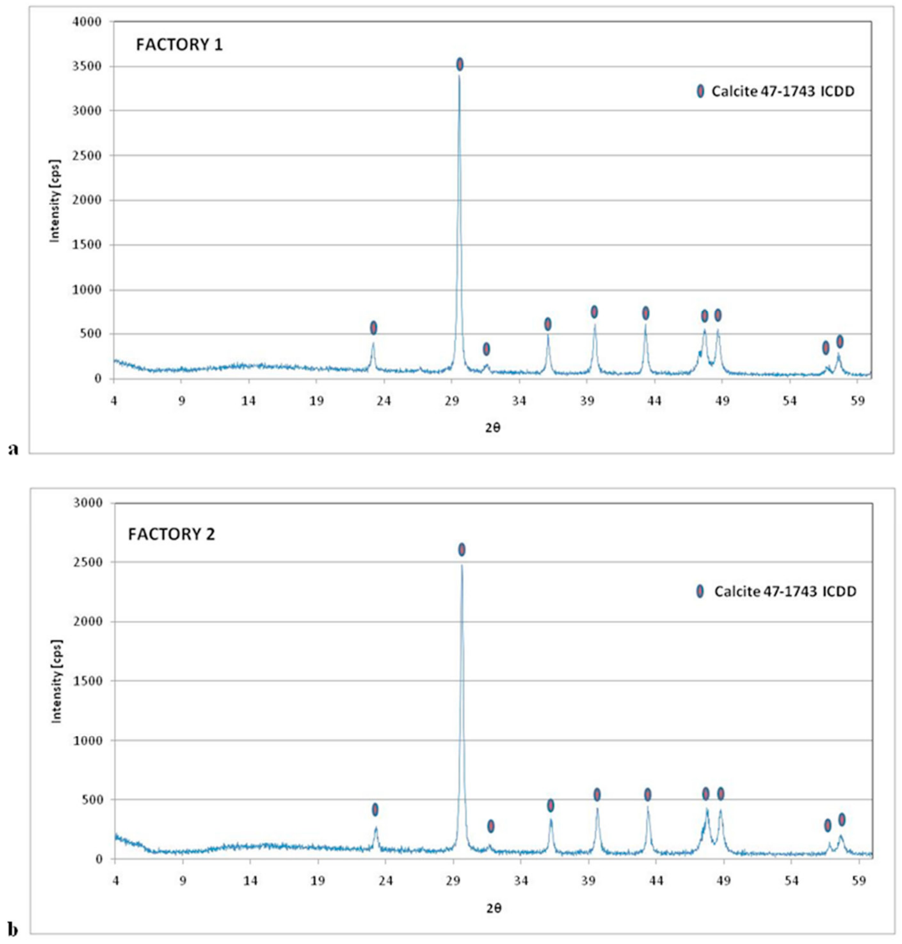

Fig. 3. (a) FACTORY 1 spectrum; (b) FACTORY 2 spectrum.

SEM images, at different enlargements, show that the particles have micrometer size (Fig. 4). This could mean that its addition should confer more cohesiveness to specific materials.

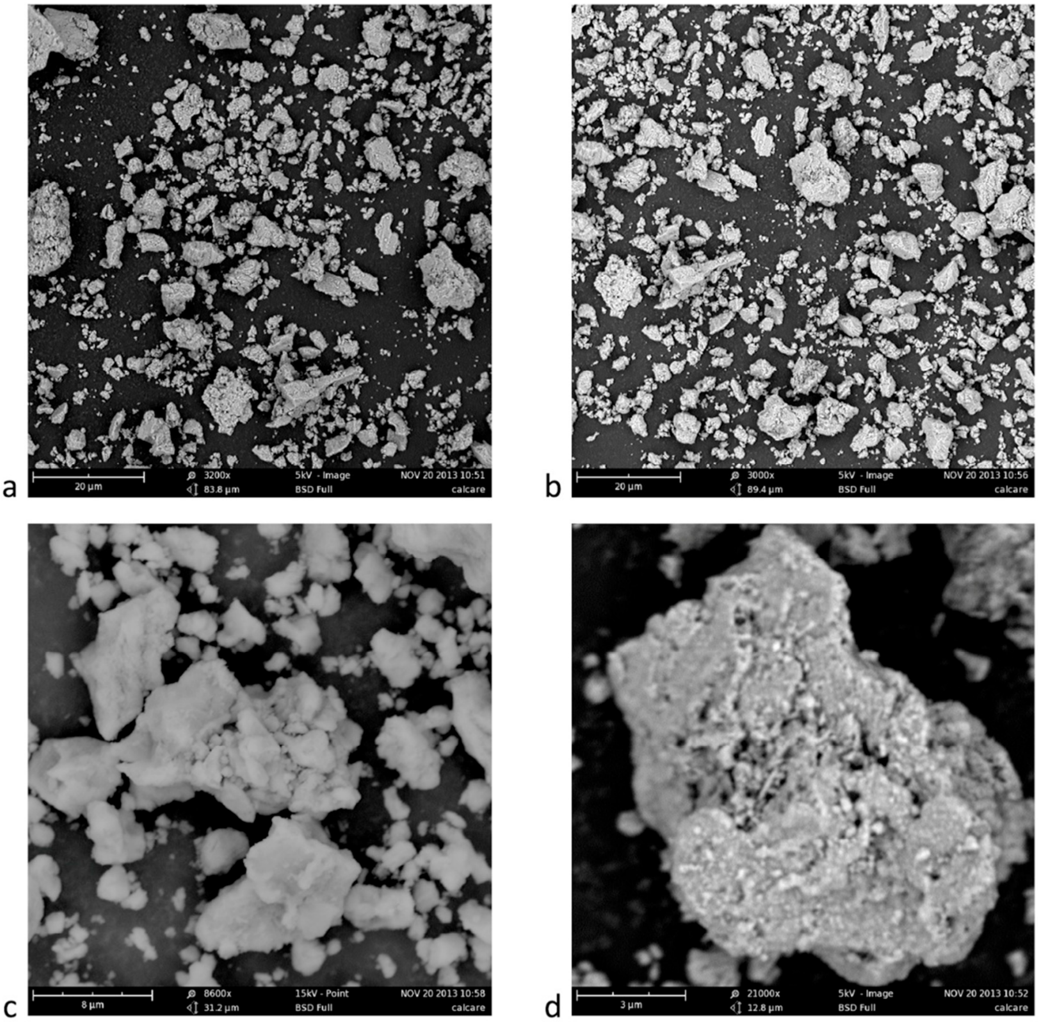

Fig. 4. SEM images (a) FACTORY 1 3200X; (b) FACTORY 1 3000X; (c) FACTORY 2 8400X; (d) FACTORY 1 21000X.

3.1. $CaCO_3$ filler and its industrial requirements

Many present-day materials and consumer goods would be unthinkable without mineral fillers. This applies particularly to the paper, plastics, paints and varnishes industries. Calcium carbonate ranks right at the top within these industries and in other areas [22]. Moreover, the market of $CaCO_3$ is a growing market, reaching 108.5 million tons by 2015 [23].

Two types of calcium carbonate filler can be detected: precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC). PCC is made by direct carbonation of hydrated lime; GCC is obtained directly from the limestone and marble by physical processes, such as crushing.

Today the criteria applied for fillers are many and varied. Depending on the branch of industry, further criteria are applied. The GCC largest market implementation is carried out by the paper segment, followed by the plastic segment. The GCC is the preferred because of its high-quality performance in the productive process and also for the brightness it confers. [3]

For this research, three different industrial sectors were investigated: Paper [24], Rubber and Tyre industries [25].

For each of the previously mentioned sectors, the calcium carbonate filler requirements were obtained from scientific literature [26] and from information provided by local companies, and they are reported in Tables 5,6 and 7.

Table 5. Comparison between values for $CaCO_3$ filler requirements in paper rubber tyre industry and marble slurries data. [WGCC: wet ground calcium carbonate]

PARAMETERS	VALUE	FACTORY 1	FACTORY 2
$CaCO_3$ [%]	> 95	99.11	99.18
Brightness ISO [%]	80 - 96	81.04	85.21
Average particles size [μm]	< 3	3.92	3.64
Particle size below 2 μm [%]	2 - 20	21.8	26.7
WGCC solids content [%]	75 - 78	74.95	75.10

Table 6. Comparison between values for $CaCO_3$ filler requirements in rubber industry and marble slurries data.

PARAMETERS	VALUE	FACTORY 1	FACTORY 2
d_{50} [μm]	0.7 - 5.0	3.94	3.72
$CaCO_3$ [%]	98.5	99.11	99.18
SiO_2 [%]	0.1- 0.4	0.14	0.16
Fe_2O_3 [%]	< 0.08	0.03	0.04
Specific gravity [g/cm^3]	2.70	2.71	2.71
Particles size < 10.5 μm [%]	82 - 90	79.1	80.3

Table 7. Comparison between values for $CaCO_3$ filler requirements in tyre industry and marble slurries data.

PARAMETERS	VALUE	FACTORY 1	FACTORY 2
Appearance	White to light grey powder	White	White
Specific gravity [g/cm^3]	2.7	2.71	2.71
Fineness - 150 μm [%]	100	99.0	99.2
Fineness - 45 μm [%]	> 95	97.8	97.8
Fineness: residue at 40 microns [%]	< 0.5	2.7	2.6
Loss in mass at 105 °C [%]	< 0.5	0.132	0.104
Loss on ignition [%]	43.50 ± 1.5	46.66	43.47
$CaCO_3$ [%]	> 92	99.11	99.18
Cu [%]	< 0.005	0.0002	0.0003
Mn [%]	< 0.05	< 0.01	< 0.01

As illustrated in the above tables, the characteristics of the marble powder obtained as a waste in the two processing plants fulfill almost completely the requirements of the possible industrial reuse as filler.

As shown in Table 5 and 6, in case of paper industry and tyre industry, the parameters values are all very close to those required. The only difference is in the average particle size, that could be reduced through a classification process. The rubber industry case shows that (Table 7) the marble powder characteristics fulfill totally the requirements and can be utilized without any previous treatment.

According to the results obtained by means of adopted characterization process, marble powder waste can be reused with no or very little further processing. The only costs of its reuse are fundamentally represented by handling and transport costs, but beside the economic aspects, the environmental benefits are the most important outcome of the operation.

4. Conclusion

The use of calcium carbonate is not restricted to the construction sector, having high demands in other industries. The highest value-added rate is achieved when rocks are ground down to fine minerals flour and powder, as in the case of marble slurry waste.

Consequently what until now was considered as a waste, can be an important economic resource capable of promoting the sustainability.

The importance of this investigation is to characterize completely the "waste" that could be reused in further processes and also to identify the feasibility of substituting marketable micronized $CaCO_3$ with marble slurry.

A comparison between chemical, mineralogical, physical and morphological characteristics of the marble powders and the requirements for raw material, in paper rubber and tyre industries, shows that the re-use of marble waste as a substitute of marketable micronized $CaCO_3$ is a real opportunity.

The benefits of such solution are of two orders. One of them is the economic benefit, due to the fact that there are not production costs for marble powder waste; that leaves even space to a possible treatment to improve the characteristics of that material. But more important is the environmental benefit that relates with the effect of the re-use of that type of waste, since it implies a reduction in the need for landfill storages and in the consequent associated detriments.

The combination of the two advantages produces a sustainability promotion and a significant movement toward a circular economy in the ornamental stones sector.

Acknowledgements

The authors are thankful to S.I.M.G. Srl and SARDEGNA MARMI, for providing the materials for the experimental phase. Gratefully acknowledges Autonomous Region of Sardinia for the financial support (L.R. of 7th August 2007 nr.7).

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