RECOVERY AND REUSE OF MARBLE POWDER BY-PRODUCT

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Abstract
The main goal of this study is to evaluate recovery and reuse of by-products coming from marble processing industries. As known, carbonate rock products have applications in most major industries, thanks to their chemical and physical characteristics. Despite this, the quarries and processing plants are littered with large amounts of waste products deriving from extraction, sawing, polishing, and water treatments. At present, no significant activities are in place to recover and reuse the ultrafine $CaCO_3$ dust contained in waste slurries of marble processing plants. It can be helpful to consider these calcareous particles as primary or secondary raw materials for use in other production processes. From this, a research is currently carried out in order to join this by-product with possible industrial applications. More specifically, a lot of analyses have been accomplished for the use of micronized calcium carbonate in paper, rubber, and tire industries. Recently, the possibility of using micronized stone powder to produce different commodities for the building industry has been studied. The investigation focused on the marble district area in Orosei (NE Sardinia). The data emerging from the analyses demonstrate the feasibility of these uses. What this indicates is the importance of enhancing this research field.

Keywords: marble dust, calcium carbonate reuses, residual sludge.

1. Introduction

Stone industry is an important factor in worldwide economy. Despite this, a large amount of residues is produced in ornamental stone industry with different dimension and particle size. The increasing rate at which raw material are continuously transformed into industrial products results in waste generation. Consequently, recycling of industrial wastes and byproducts is becoming a crucial demand by the environmental laws in agreement with the concept of sustainable development.

As known, there is a diversification in waste generation as the following one: waste deriving from quarries and offcut/waste deriving from processing plants. Moreover, there are two types of natural stone processing waste: solid and semi-liquid or slurry (Almeida et al., 2007). In fact during the marble cutting process by gang saws, water is used as a coolant and the powder flows along with it as waste marble slurry.

Depending on the kind of process involved, the sludge generated is equal to between 20-30% of the weight of the stone worked (Bertolini et al., 1990). Deposition in landfill is the most current destiny for these residues.

Marble dust has various industrial uses, in fact thanks to the high percentage of fines and the low percentage of metallic oxides, the ultra-fine calcareous particles could well be recovered and marketed for a number of industrial applications that employ micronized calcium carbonate.

These include: agricultural soil amendment, manufacture of cement (Misra & Gupta, 2008), filler in the manufacture of various types of paper, paint, and polypropylene, production of soda, blast furnace flux, acid neutralizer for industrial effluents and for heavy metal sorption (Pincomb & Shapiro, 1994), flue gas desulphuration in electric power stations (Fraes, 1994), manufacture of lime, resin conglomerates for flooring and coatings in the building industry, a multitude of chemical applications, including cosmetics and pharmaceuticals. It is also used as filler in concrete and paving materials. The recycled sludge can be also used as whitewash, in paint, as filler for electric insulators or industrial filters (Industrial Minerals HandyBook, 2002). All these uses provide a valuable apply for what is otherwise a waste material.

By far the most effective and widely applicable option is to use the waste in civil and mining engineering works.

In Sardinia (Italy), even if granit is the main dimension stone produced, marble is a productive sector too. The area object of this research comprises the extractive district of

Orosei in NE Sardinia where limestone abounds and known in trade circles as *Orosei Marbles* though this term is not strictly correct (Siotto et al., 2008).
The limestone deposit quarried for dimension stone is of Mesozoic age. The NE-SW elongated Monte Tuttavista massif is composed of thick calcareous and dolomitic sequences that formed during the Jurassic and Cretaceous. The basal part of the carbonate sequence is composed of brown dolostone interbedded with arenaceous limestones, passing upwards to well-bedded light coloured limestones (Siotto, 1999).
The processing facilities are situated in the same area which has been designated both as an extractive district and industrial pole. This zone extends over 200 hectares; 15 quarries and 15 processing plants currently operate therein. The processing plants handle 65% of the entire quarry production. There are also about 400 skilled workers employed in the district.
It should be noted that, just in Orosei Marble District (NE Sardinia, Italy), factories produce approximately 60,000 m^3/year of carbonate ultra-fine particle, currently disposed of in the council waste site for inert materials (Careddu et al., 2009).
The present study aims at showing how environmental burdens in conjunction with stone production could be reduced to a minimum identifying possible marble dust reuses as by-products.
The investigated sector is the building one and the goal focuses on the possibility to use marble dust for obtaining bricks.

2. Materials and method

2.1 General

Marble sludge was supplied by S.IM.IN. s.r.l. which operates limestone quarries and stone cutting facilities in the area. This enterprise is one of the members of the Orosei Marble district. Its plant is equipped with both block cutters, milling cutters and also with a sludge water purification system. Clays were supplied by INPREDIL S.p.A..

2.2 Materials and equipment

2.2.1 Calcium carbonate dust characterization

As written before, experimental programme is finalized to study the effect of addition of marble powder on the properties of bricks. Firstly, were carried out physical, mineralogical and chemical determinations in order to characterize the marble dust. Secondly, test specimens were prepared in the INPREDIL laboratory by direct mixing of two kinds of clays with marble powder in different proportion. A marble dust sample brick was subjected to the same stage of firing suffered from the test specimens.

2.2.1.1 Grain size distribution and bulk density

Grain size analysis was conducted on the dry solid cake produced by the filter-press using a *Sedigraph 5100 Analyser*. Grain size distribution is shown in Figure 1.

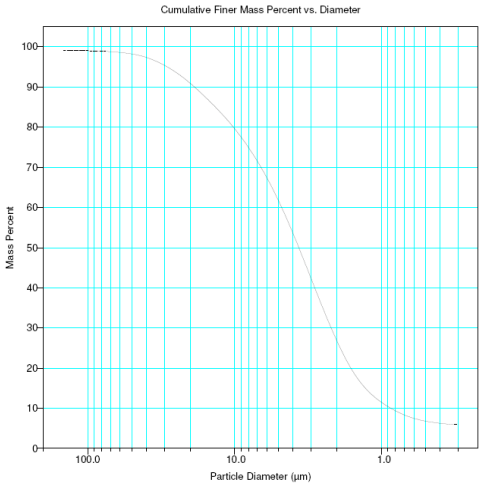

Figure 1: Grain size distribution SIMIN filter-press sample

Bulk density of a representative sample of the filter pressed material in the processing plant was determined using an Accu Pyc 1330 gas pycnometer manufactured by Micromeritics Instruments (Table 1).

Table 1: Density dry solid from filter press

SAMPLE	Density [g/cm^3]
SIMIN sludge	2.66

2.2.1.2 Mineralogical analysis

X-Ray diffraction (XRD) analysis was performed on the dewatered slurry to determine mineralogical composition (Figure 2).

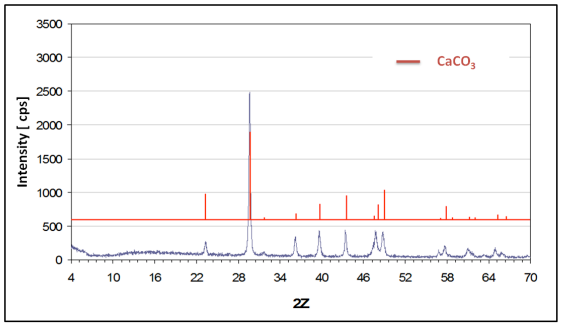

Figure 2: XRD filter-press sludge spectrum

Mineral phases were determined by comparison with the JCPDS index (JCPDS, 1985).

2.2.1.3 Chemical analysis

The technique used for the preparation of the solutions was lithium metaborate fusion. This provides a method for preparing solutions suitable for rapid methods of analysis (Panteeva, 2003). The sample (0.5 g) was carefully mixed with 2.5 g of lithium metaborate in a clean platinum crucible. Samples were fused in a muffle furnace at 950 °C for 45 min. When the fusion was complete the crucibles were removed from the furnace and allowed to cool. The crucibles were placed in a tall 150 ml beaker. Teflon coated stirring bars were placed in the crucible and 125 ml of 10.1% v/v nitric acid solution was added. The beakers were place on a plate stirrer; solutions were then filtered into 250 ml volumetric flasks and made to final volume with distilled and deionised water. The blank was prepared by performing the sample preparation without any sample present. The final dilution factor was 400.

After that, to read major elements five milliliters of each sample solution were further transferred into a 10 ml glass bottle and made to final volume with the blank. The final dilution factor was 800.

The solutions were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) manufactured by Varian (Varian 710-ES).

The loss on ignition determination was made by weighing 3 g of test material into a crucible, heating slowly from room temperature to 1000°C, maintaining this temperature for 16 hr. After cooling in a dryer for 3 hr, the percentage weight loss was calculated (Ramsey, 1995).

The data of chemical composition and relative proportions in oxides and loss on ignition are summarized in Table 2.

Table 2: Major components

COMPONENTS	SIMIN SLUDGE [%]
LOI	42.62
CaO	54.07
MgO	0.60
SiO_2	0.43
Al_2O_3	0.14
Fe_2O_3	0.05

2.2.2 Clays characterization

In this study were used two different types of clays: black clay Ussana (BCU) and the yellow clay Monastir (YCM). Representative samples of these two clays were analysed by chemical, grain size analyses (omissis) and Atterberg limits. The data of chemical compositions and Atterberg limits for both samples are presented in Tables 3 and 4.

Table 3: Chemical data for the two clays

COMPONENTS	YCM [%]	BCU [%]
SiO_2	56.00	63.66
Al_2O_3	11.40	15.95
TiO_2	0.65	0.92
Fe_2O_3	5.63	8.30
CaO	8.63	0.41
MgO	2.13	1.64
K_2O	3.53	4.00
Na_2O	0.74	1.00
S	0.002	nd
Fl	0.071	nd
Cl	0.023	0.48

Table 4: Atterberg limits

	Lp	Ll	Ip
BCU	19.8	39.1	19.3
YCM	21.2	32.4	11.1

2.2.3 Preparation and casting of test specimens

For this study were made different mix-designs by direct mixing of the black clay Ussana and the yellow clay Monastir with marble dust (MD) in different proportion, varying in percentage (Table 5). The clays were previously sieved to 200 mesh sieve. The YCM gives the brick structure so the percentage of marble powder added was simultaneously removed from BCU. In the following table are listed the mix-designs:

Table 5: Mix-designs

MIX-	YCM	BCU	MD	WATER
A	50	40	10	17
B	53	40	7	16.7
C	55	40	5	16.8
D	57	40	3	16.3

Mixes were prepared, thanks to a paste mixer, by inserting the different percentages of the three components with the addition of water vary depending on the workability. The paste had a starting weight of 1 kg to achieve a final sample of approximately 400 g.

The paste bricks were cast inside molds with dimension of 12x8.5x2 mm.

Mix-design C was chosen as the sample to be submitted to subsequent analysis because for the other mixes there were problems related to drawing due to the segregation between the various components during preparation of the paste.

Two notches were thus engraved on the mix-design C surface by a digital comparator in order to check the shrinkage, at the end of the two processes (drying and firing); notches distance was 5 cm and placed along the greatest dimension (Figure 3).

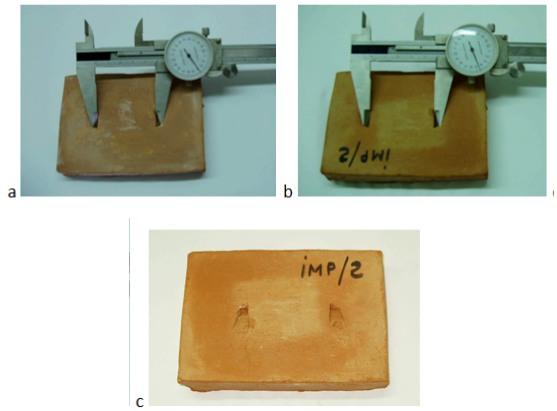

Figure 3: Brick sample post-drying (a), post-firing (b and c)

2.2.4 Specimen analyses

The final trial brick was introduced for 8 hours in the dryer (T 130°C).
At the end of this treatment, it was analyzed for the shrinkage and weight variation.
Further processing was sample firing for 36 hours inside a tunnel type furnace with a curve that had consistently led the sample from room temperature to 850 °C.
Even after this step, was immediately observed shrinkage from the sample, related to the drying phase.
Regarding the calculation of specific absorption rate (a_s, imbibition, UNI 8942-3), the sample C was allowed to cool in order to identify its mass M1 and to measure the gross area of the bearing surface F_0. The imbibition was determined in according to the following equation (1):

$$a_s = \frac{G_2 - G_1}{F_0} \quad [\text{g}\cdot\text{min}^{-1}\cdot\text{dm}^{-2}] \quad (1)$$

In addition, the water absorption (w_a) capacity was obtained by immersing sample C in water for 48 hours. The value was determined by the formula (2) where W_1 and W_2 are respectively the weighs before and after immersion.

$$w_a = \frac{W_2 - W_1}{W_1} \quad [\%] \quad (2)$$

3. Results

Calcium carbonate dust characterization showed that the particles are very fine, as resulted in the grain size curve. The main fraction of the material exhibits grain sizes of below 25 µm (Figure 1). The XRD spectrum shows calcite to be the only mineral constituent detected (Figure 4). The marble waste dust contains very minor amounts of impurities; therefore there are no constraints in adding MD as by-product.
The marble dust sample brick subjected to the same procedure of firing used on the mixed-specimens, has reached the workability with the addition of 26.9% water.
Was measured the shrinkage after drying, equal to 4.20 % and, even after firing, the value of which was 1.88 %.
Moreover, spent two hours by cooling, the sample was crumbled. In fact, the calcium carbonate after firing has turned into lime which consecutively at room temperature became hydrated lime as shown in Figure 4.

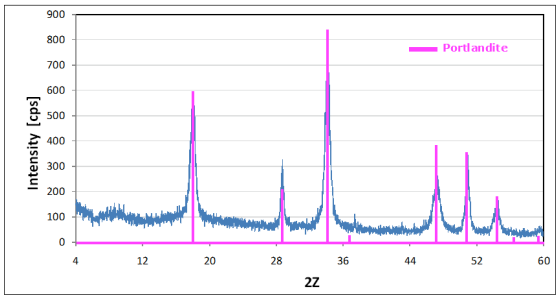

Figure 4: marble dust XRD spectrum after firing

As regards C, after drying, the shrinkage was measured equal to 5.60 % and after firing the value of which was 0.42 %. Moreover, the specific absorption rate was checked equal to 0.31 $\text{g}\cdot\text{min}^{-1}\cdot\text{dm}^{-2}$ while water adsorption percentage was 13.8 %. It is important noticed that a standard brick made by INPREDIL S.p.A. has the following values: a_s = 0.37 $\text{g}\cdot\text{min}^{-1}\cdot\text{dm}^{-2}$ and w_a = 14 %.
As seen from the results, the sample C water absorption is just a little bit lower than the standard brick one, and since the water absorption is one of the most critical properties for bricks, a small decreasing in this factor is a positive consequence.
Results show that paste prepared with marble powder, and that using 5% of MD in bricks could be well considered, as a matter of fact the outcomes are very hopeful for mixing the marble dust in the conventional bricks making.

4. Conclusion

The sludge produced in the Orosei district is a nearly pure carbonate having a micrometer size. For this reason the waste can be considered as a product with high added value that can be applied in various industrial fields. In the specific case of this research the use of MD along with the other traditional constituents has resulted in improvement of quality of bricks. The result is very encouraging for mixing MD in the brick manufacturing; in fact it can partially replace clay, pursuing the aim of lessening waste generation and disposal and also of producing revenue for enterprises.

Nevertheless the study is ongoing and needs to be supplemented with mechanical studies.

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