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TITOLO TESI

Recovery and valuation of ultrafine marble dust contained in waste slurries deriving from carbonatic natural stones processing plants

Settori scientifico disciplinari di afferenza:
ING-IND/28 Ingegneria e Sicurezza degli Scavi
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This thesis is dedicated to my
family and to all those who
believe in me … but mainly to
my nephews Gabriele,
Donatella, Michele, Valentina e
Nicole that I adore.

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INTRODUCTION

Every stone material used in such projects originates from quarries and undergoes a long “story” before it can become a finished product: research, study, quarry work, technical tests and, lastly, processing and finishing to meet in full the technical and aesthetic requirements of each kind of application (Primavori P., 1999).

The term *dimension stone* used in Italy is matched by *dimension stone* in English and *piedra natural* in Spanish.

The subject of this dissertation was emerged with the worldview from the perspective of sustainable development, as set by the “Report of the World Commission on Environment and Development” (United States, 1987). This term was used by the Brundtland Commission, formally the World Commission on Environment and Development, which coined what has become the most often-quoted definition of sustainable development as development that “meets the needs of the present without compromising the ability of future generations to meet their own needs”.

The success of economy of the Countries depends on the building sector, for the most part, and on the large civil construction works. The building development of the industrialized countries must necessarily give priority to environmental conservation, we must not fall into the grave mistake of promoting only the productivity, such as in emerging or developing countries, in which the environmental degradation and the gradual pollution reflect negatively on the health of everybody.

Building activity is closely linked to the supply of raw materials and, all over the world, the two main categories of general natural stone are: siliceous materials (granites + sandstones + slates) and limestone materials (limestones + marbles). Traditionally materials like clay, sand, stone, gravels, cement, brick, block, tiles, paint are being used as major building components in construction sector. All these materials have been produced from the natural resources and thanks to their extraction.

As known, natural stone sector involves a high production of residues, of varying shapes and sizes, deriving from extraction and processing,. In the stone manufacture industries, a huge quantity of wastes are being produced which give problems for long time landfill. These kind of residues are considerate such as an inert waste and usually they are depose in landfill; furthermore, the main objective of the Integrated Waste Management System is to consent an environmentally and economically advantageous way to sustain the continuous increasing volumes of waste products.

To avoid the increase amount of waste it is necessary to find alternative ways such as the reuse or recycling. Nowadays, most researches are focused on determining a strategy to reuse/recycle the material residue of the construction sector. It can be used as an alternative material in the applications of civil and industrial engineering

The reuse of the finest section of this residues recovered at the exit of the filter-press section, instead of representing an economical extra-charge for the companies due to its disposal.

Then aim of this doctoral thesis is the identification of the possible reuses/recycling options of the sludge produced by the plants in the *Orosei Marble District* in building sector.

Fig. 1: Orosei Marble pole aerial - view (Siotto, 2006).

Marble is the larger natural stone exploited, in fact the marble has approximately 50 % share of world stone production (Bhatnagar, 2009).

The term “marble” derives from Latin word “marmor”, which itself comes from the Greek root “μάρμαρος” meaning thereby a shining stone. Petrographically marble is a recrystallised (metamorphosed) limestone. In commercial terms, marble is any crystalline rock composed predominantly of calcite, dolomite or serpentine, having 3 - 4 Mohs hardness, which can be excavated as blocksand; it can be sawed and takes good polish.

Amongst the building stones, marble occupies a unique position. Since time immemorial, marble has been used in temples, mosques, palaces, monuments, as well as an ornamental and decorative stone. Merble has pleasing colours, attractive patterns and designs. Suitability of marble for any purpose does not depend on chemical composition or genetic aspect, but on its physical properties which is fascination for its colour, shade, luster and design preferred by the user.

Generally, the Marble is exploited in blocks and have to be processed to make them suitable for the end users. Other than quarrying waste, there are processing waste deriving from operations like sawing, with diamond wire, slabbing, polishing etc. Basically, there are two types of natural stone processing waste: solid and semi-liquid or slurry (Almeida et al., 2007).

Stone slurry generated during the processes, corresponds at 40 % of the initial dimension stone mined, even if this value depends on the technology availability. This sludge is composed primarily of calcium carbonate and has a great potential as secondary raw material or byproduct The calcium carbonate has a great importance not only in the construction sector as well as other important industry (e.g. environmental, food, pharmaceutical, industrial, construction). It is used in the form hydrated lime or micronized products.

Processing residue is classified under Italian regulations as special waste. These by-products are coded in the European Waste Catalogue as 010413 “waste from stone cutting and sawing other than those mentioned under item 010407”.

Ultrafine particles have up to now been considered as waste and treated as such by their producers consequently finer size fractions are still accumulated in the council waste site for inert materials.

Actually there is the necessity of appreciate the potential value of Marble and convert it into *marketable* products, thus doing away with the costs necessarily incurred by the extractive industry for its disposal.

The experimental phase was conducted by characterization of the Orosei Marble sludge, and several tests to evaluate the feasibility of the reuse/recycling in some production processes.

A first step consisted in the study of the previous literature, The second step was collect samples in the five companies selected for the research belonging to the Orosei Marble District: S.I.M.G.$_1$ s.r.l., S.I.M.G.$_2$ s.r.l., S.IM.IN. s.r.l., De.Da. s.r.l., Marmi Daino Real s.r.l.. A representative sample was physically, chemically and mineralogically characterizated (Chapter 4); and finally the experimental tests to evaluate the potenzial reuse were carried out.

The tests used in this study were the following:

- Comparison with industry specifications for paper, rubber and tires (Chapter 3).
- Preparation of concrete specimens adding marble dust as a substitute of the cement for testing compressive strengths (Chapter 5).
- Forming of structural elements in brick adding marble dust, thanks to the cooperation with the INPREDIL company (Chapter 6)
- Preparation of gypsum plaster specimens, adding marble dust in different percentage, for testing flexural and compressive strengths and for determining the adhesion (Chapter 7).
- Preparation of experimental cellular blocks for the production of cellular elements of lightweight concrete (Chapter 8).

The experimental work was executed during the Ph.D. course, in the Department of Geoengineering and Environmental Technologies, University of Cagliari, with the support of the Department of Geology Engineering – Higher Technical School of Mining Engineering - Technical University of Madrid. In addition, the experimental phases was carried out in the laboratories of the same Departments and also thanks to the CNR-IGAG of Cagliari, to the LOEMCO laboratory in Madrid, and thanks also to the companies mentioned above, in partial fulfilment of the requirements for the Ph.D. degree.

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1. GEOLOGY OF SARDINIA

Sardinia ranks second in size among the Mediterranean islands. Its geographical configuration features low mountainous reliefs which are the result of processes of rock erosion started in the Ancient Paleozoic. For this reason rocky plateaus of granite, basalt, trachyte are predominant and their altitude ranges between 300 and 1,000 m a.s.l..

The ancient geological history of Sardinia, reconstructed through the analysis of the outcropping lithotypes and the correlations with other areas of central and western Mediterranean basin, distinguishes it from the remainder Italian territory and explains why its 24,000 km^2 of territory retain substantial traces of almost all geological ages, offering a sampling of wide range of rocks of valuable varieties.

The Sardinian rocks can be dated, with certainty, what the oldest date back to the Lower Cambrian, which represents the beginning of a succession, ending between the Carboniferous and Permian. This Paleozoic sequence (currently metamorphosed but originally formed by sedimentary and volcanic rocks) was involved in the Hercynian Orogenisis, following which more than 300 million years ago, produced the granitoids, which is currently emerging in large part of the island.

The old basement of Sardinia is therefore made up of granitic rocks and of metamorphosed products of Paleozoic sediments and volcanic rocks.

In the following ages, ranging throughout the Mesozoic and Early Cenozoic, there is the almost total flooding of the basement (with only brief periods of emergence) and the subsequent deposition of large quantities of limestone, the area witnessed by numerous plateaus and the Jurassic ones are exploited for ornamental stones.

In the Middle Cenozoic new tectonic events occurred, mainly extensional ones, that generated the Sardinian rift; the volcanic phase related to these events, led to the emplacement of all pyroclastic rocks and of some lave currently marketed. The last part of the Cenozoic Era marks the end of the crustal movements; after a period of stagnation, however, there is the beginning of a new relaxation phase (which lasted from the late Tertiary and Early Quaternary, especially in central-southern Sardinia). Sardinia is the most important Italian region for the presence, on its territory, of granite mass, the granitoid intrusive rocks, extending, in fact, for about 1/5 of over 24,000 km^2 of the surface region: this gives the island great potential in terms of development of mining, although the Sardinian granite is strongly affected by cataclastic phenomena, for which the high probability of internal fractures often prevents the extraction or the commercialization. In view of these factors, a rational and accurate resource could lead to development of the sector in the medium-long with wide margins.

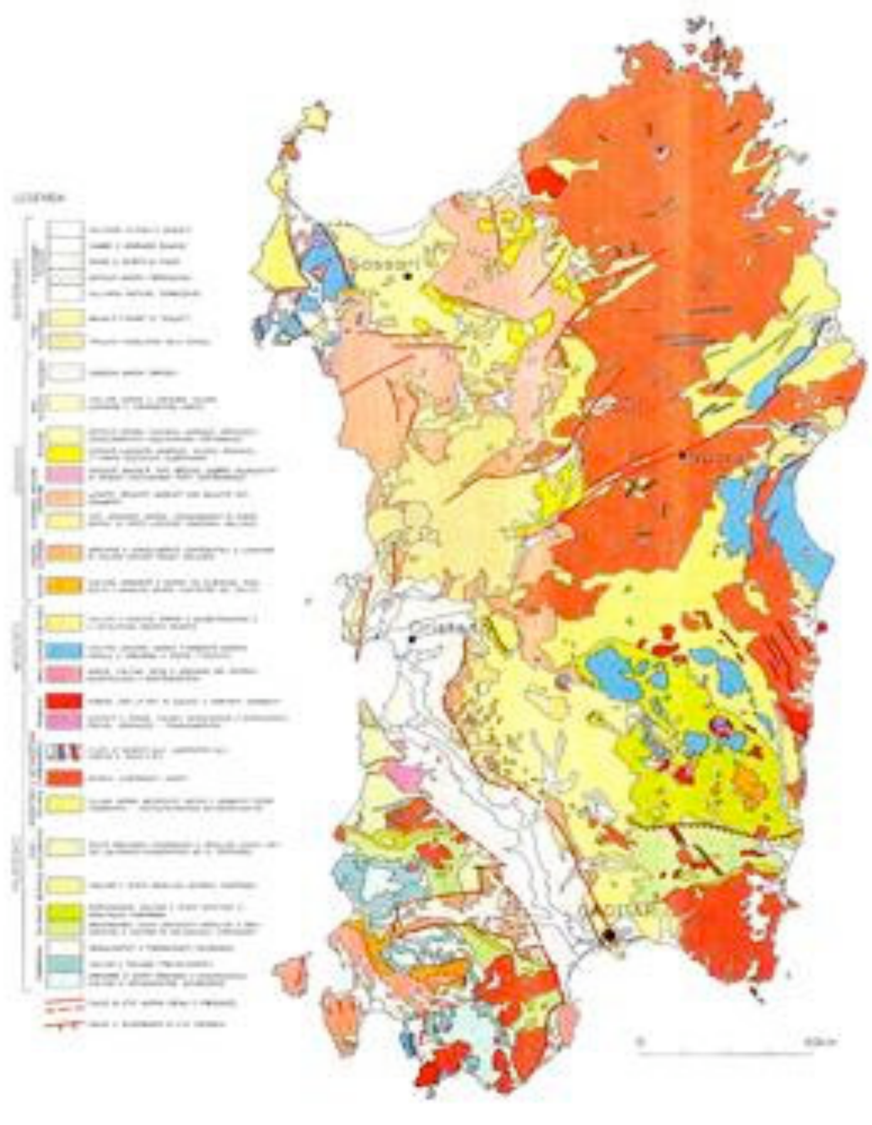

Fig. 1.1 : Geological Map of Sardinia.

1.1 Orosei Marble District

1.1.1 Generality

Orosei Marble District has been awarded by the Italian Government as one of the four Sardinian industrial districts and the Autonomous Region of Sardinia has recognized as one of the four extraction areas of ornamental stone in the island.

1.1.2 Orosei Geographical Context

Orosei is located in the Cedrino River valley on the centre-east coast of Sardinia and is the chief town in Baronia. It can be reached through two main roads: the *Orientale Sarda* s.s.129, which connects Orosei and the port of Olbia and the *Traversale Sarda*, which connects it to Nuoro and the rest of the island. The place is on one of the most suggestive gulfs in the Mediterranean Sea. The splendor of its sandy shores and its crystal-clear waters make it one of the greatest tourist attractions of the island.

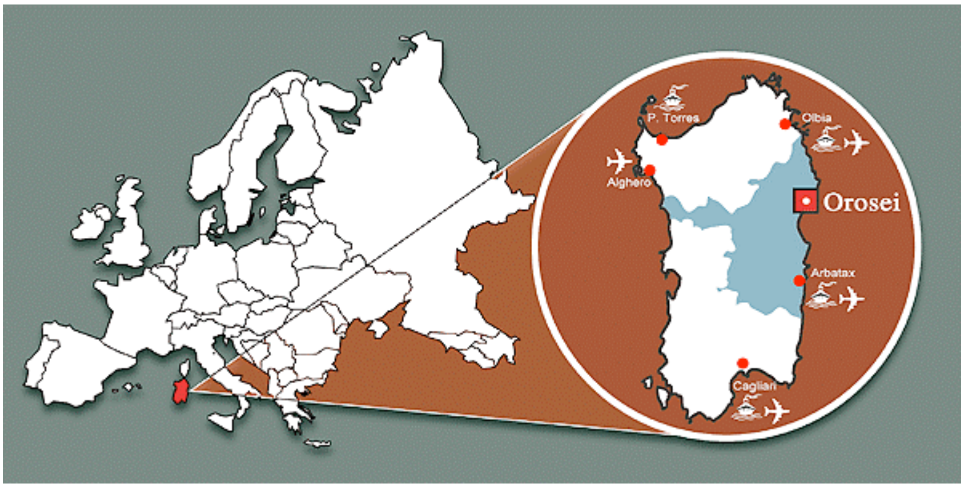

Fig. 1.2: Orosei geographical location (Siotto, G., 2006).

A Roman colony starting from the 3rd century B.C. until the empire, in the Middle Ages it had its centre built where it still is nowadays: the castle and the port, which allowed trading with the peninsula, bear witness to the special importance it gained in the 14th century, from a strategic, military and commercial point of view. It was under the Pisan and Aragonese domination until the 15th century, when it passed under the rule of the Guiso Barons. Due to malaria and the decrease of commercial exchanges caused by recurrent pirate raids, the small town met a slow decline until the mid 1800s. Thanks to interventions such as the bridge on the Cedrino River (1876) and the reclamation of the valley, the place is today involved in an economic development of high relevance, regarding the agriculture, handicraft and tourist sectors. In a perspective of an integrated development of the territory, it is revealing to say that Orosei is within the *"Parco del Gennargentu e del*

Golfo di Orosei" and is also part of the *"Parco Letterario Grazia Deledda"* together with the neighbouring village of Galtellì.

Fig. 1.3: Orosei marble district view - CTR Map - 1:5000 (Siotto, G., 2006).

1.1.3 The marble deposit of Orosei

In the vast territory which includes the administrative boundaries of the five municipalities of the *Bassa Baronia* (Orosei, Galtellì, Irgoli, Onifai and Loculi), represented in the Geological Map at F.º 195 – Orosei, there are several deposits of ornamental rocks that represent the most important natural resource, as part of raw materials, of the ex-10th Mountain Community of *Baronie*.

With reference to the main ornamental quarry materials, located in *Bassa Baronia*:

- The polishable limestones of Mount Tuttavista, subject of this report, which the borders including the municipalities of Orosei and Galtellì.
- The ornamental pink cutting granite of Onifai and Orosei, the gray-pink ones of Irgoli.
- The basalts of Galtellì and Orosei, used as cutting blocks to be valued in the form of blocks, strips and solid pieces, strips and ornamental slabs and as dimension quarry *tout-venant* for the production of building materials (road foundation, aggregates for cementitious and bituminous conglomerates).

- The Quaternary formations of materials for industrial uses located in many parts of the territory of the ex-10th Mountain Community: the slope debris and landslide, more or less cemented, of Monte Tuttavista; recent alluvial materials, the terrace alluvia, mainly the pebbly one of Galtellì; the sandy and plebby and the like.

The polishable limestones of Mount Tuttavista constitute, by extension and volume of reserves for explotation, the most important marble deposit (as seen in its broadest commercial sense, as known generally in the international market as "Orosei marble") of Sardinia; quarrying has so far affected, almost exclusively, the lower slopes of the mountain, oriented east-southeast, in the area of *Canale Longu* and *Oroe* (Municipality of Orosei), in which numerous quarries operate, many of them for about thirty years.

Orosei Marble is extracted from Monte Tuttavista (850 m a.s.l.). The field is around 300 hectares in size with a depth of 560mt. ca. presently it is exploited for 6% of its ascertained reserves.

The sludge, used in the investigation, is drawn in the Orosei extractive area (NE Sardinia). In this extractive marble district limestone abounds and the local stones are known in trade circles as Orosei Marbles though this term is not strictly correct, from a petrographic point of view.

The limestone deposits quarried for dimension stone are 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 (Fig. 1.4) . 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, G., 1999).

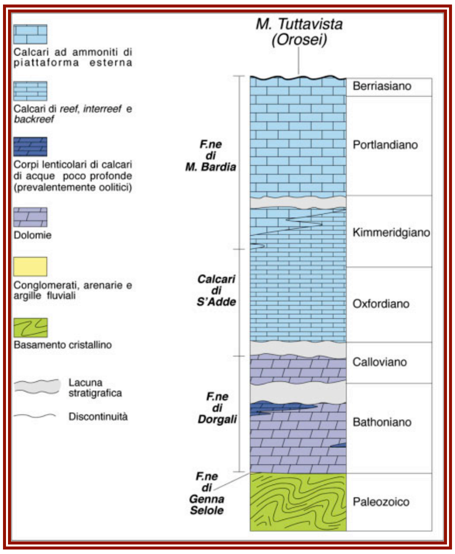

Figure 1.4: Orosei deposit's stratigraphic column (Siotto, G., 2006).

The processing facilities for the Orosei stone are situated in the Industrial Zone D which has been designated both as an extractive district and an industrial park. This zone extends over 200 hectares (around 500 acres) and 15 quarries and 15 processing plants currently operate therein. The processing plants handle 65% of the entire quarry production.

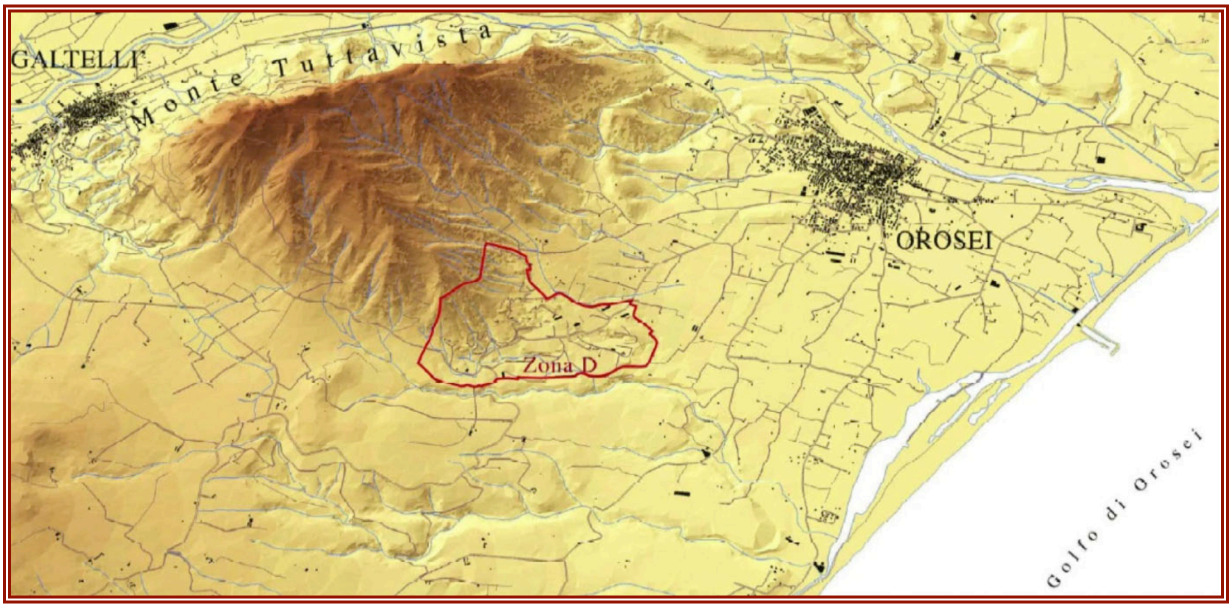

Figure 1.5: Orosei Marble pole's prospectic view (Siotto, G., 2006).

General Recovery Plan for the whole production sector was presented in 2006. The document describes also the evolution of quarrying until 2055 (Siotto, G., 2006).

1.1.4 Geological and depositional characteristics

1.1.4.1 Stratigrafy

As is clear from the Geological Map of Italy, F° 195 - OROSEI, the series of outcrops in the studied area is made up by the following formations:

- Paleozoic crystalline basement: metamorphic schists and magmatic epifacies, of uncertain age, Hercynian granites, normal type (white granite) and pegmatitic (pink granite), with micro-granites, aplitic and lamprophyric seams and quartz veins.
- Rhyolitic ignimbrites with intercalated sandstones and Permian conglomerates.
- brown and grayish transgressive dolomites (Middle-Late Jurassic), usually massive, resting on the basement, directly or through clastic layers in fluvial-lake and coastal environment.
- "Formation of Dorgali" by Amadesi, Cantelli, Carloni and Rabbi (1960).
- Brown colour stratified limestones, sometimes oolitic and pseudoolitic ones of hazel brown colour, but mostly very fine grained, the *Kirneridgiano* (Later Jurassic).
- Organogenic compact limestones of bioherma (cliff) of Later Jurassic, white coloured, often moving on bioclastic limestones with lithological types similar to those on the lower levels.
- Limestone, calcareous and arenaceous marls, and pudding-stones to nummulite etc (Middle Eocene).
- Polygenic conglomerates with chaotic crystalline and calcareous elements of the Oligocene-Late Eocene.
- Sands and foraminifers, corals, brachiopods, molluscs of Early Pliocene.
- Sandy and pebbly alluvia, ancient alluvial cones and deltaic pre-basaltic deposits of the Early Quaternary.
- Layer and landslide debris cemented with limestone and dolomitic blocks (Early Quaternary).
- Monogenic chaotic mega-breccias, with limestone elements strongly cemented (Early Quaternary);
- Alluvial detrital cones with large blocks and ancient alluvia, more or less cemented, deeply incised by erosion (Early Quaternary).
- Olivinic-augitic basalts (Early Quaternary).

- Alluvial cones with angular elements and ancient pebbly alluvia (Middle Quaternary).
- Fossiliferous sands and gravels (Middle-Late Quaternary).
- Alluvial detrital cones with very small gravel with uniform granulomentry (Middle-Late Quaternary).
- Incoherent or poorly cemented layer debris (Late Quaternary).
- Alluvia and coastal dunes (Nowaday).

1.1.4.2 Tectonic

Schists of the crystalline basement have been intensely folded and metamorphosed by the Hercynian orogenesis (Middle Palaeozoic), during which was formed the white and the pink granite.

The deformations have taken place with a tight isoclinal folding, folds with E-W direction and South immersion, or, according to another interpretation, with a large anticlinal fold with the gneiss in the centre.

Starting from the intrusion of granites, the main tectonic directions take the NE-SW trend, corresponding to the direction of the seams.

The Jurassic and Cretaceous formations and, in particular the Mount Tuttavista, have been affected by the subsequent Alpine orogenesis, with tectonic fracture second main directions NE-SW and locally N-S, distorting also the Eocene and Pliocene deposits, resulting in intermediate stratigraphic gaps that correspond to periods of emersion and erosion.

1.1.4.3 Morphology

The dominant element in the Orosei Galtellì and Orosei’s area and is given by the Mount Tuttavista, that is elongated second the NE-SW tectonic director, emerges strongly on the crystalline Paleozoic formations to the north-west, on Quaternary basalt plateau to the north-east and south, on alluvial flat land to the east.

The southern side, engraved in banks with direction of the dip to east, it connects smoothly with the coastal plain by a band of piedmont debris of the ancient and modern Quaternary, while the northern slope rises from the tectonic valley of the Cedrino, bordered by ancient landslides blades rock, and dolomitic and limestone cemented blocks.

Further north, in the territory of Onifai, the pink granite is molded in low relieves by gentle slopes, formed by a mantle of sand, from which stand out from the fragmented blocks, fractures of various types, sometimes with characteristic forms produced by tafoni erosion. Harsher and more varied is the morphology of white granite, which appear more intensely fractured.

On the granite sometimes rise, as walls that break the uniformity of the morphology, micro-grain quartz veins.

1.1.5 Orosei Marble

The term marble is used in petrography to indicate a metamorphic rock made up of calcite, dolomite and/or aragonite for 50% of its volume at least. Metamorphic rock means that a change has occurred – from an initial state of limestone to marble - following a crystallization process due to high temperatures. By “marble” we technically refer also to carbonatic rocks (limestone and dolomites) even though of a non- metamorphic origin. The main features of marble are its homogeneous grain veins, ranging from medium to coarse, together with its colour, which is in relation to the degree of metamorphism: the higher the metamorphism attained, the paler the rock. Besides, the variety of shades is also in relation to the presence of extra minerals: hematite, chlorite, goethite, bituminous substances. Orosei Marble is the marble extracted from Mount Tuttavista (850 m a.s.l.) and covers a piedmont area of around 300 hectares with a depth of around 560 m. The mountain features Mesozoic limestone and dolomitic portions of layers from the Jurassic and Cretaceous age. It is exactly the widespread limestone Mesozoic rocks that count among them types of marble as follows: light, veined, cloud-like of different shades and veins. The extraction activity and the working of marble thrived in the 1960s and developed to become a significant industrial reality in centre-east Sardinia. To get an idea about it suffice it to say that the yearly production of marble blocks is 300,000 cubic metres ca. and the number of employees in the works is about 450 skilled workers and more than 1,000 with its suppliers. The growth of the sector is favoured by the dynamism of businesses that aim at promoting Orosei Marble in the world markets, guaranteeing quality and good value prices of the product. After about 30 years of extraction activity only 30% of the reserves in Orosei have been exploited and only around 30 hectares regard the quarrying activities. The long life and great value of the product need not be proved but it is useful to remind that the world consumption of stone materials has gone up from 240 million sq. m. in 1981 to 600 million currently, with a growth rate of 8 % per year.

1.1.5.1 Orosei Marble - Processing techniques

Marble quarrying and processing within the Orosei Marble Industrial District is carried out using technologically advanced plants and machinery. During the excavation stage both diamond wires and chain-saws are used. The first ones are used to vertically cut and square the blocks, the latter are used to horizontally cut portions of layers at their bases.

Within the quarry, blocks are moved around and transported using mechanical shovels, excavators, dumpers and powerful derricks.

The processing of the blocks is carried out with the following machinery: diamond looms for sawing slabs; diamond disc block-cutters are used for working on strips and tiles; complex processing lines are used to chamfer marble-chip tiles and to manufacture “modulmarmo” and “zoccolino”. Businesses are also equipped with plants for resining slabs, several types of milling cutters and water-jets to carry out finishings and special workings.

Moving materials inside production factories takes place using stand cranes for blocks and lift trucks for finished and semi-finished products.

It is necessary to underline that all businesses belonging to Orosei Marble Industrial District always reclaim industrial waters used during the processing stages; for this purpose suitable closed- cycle purifying plants are available. The use of the machinery and the plants described above has enabled to improve production techniques and has allowed the making of thinner strips, it has also allowed the use of backing materials, with sure advantages with regard to saving and lightness of the finished products; obviously, such advantages have repercussions on laying and transport.

1.1.5.2 Orosei Marble - Types

The presence or lack of veins, the colour the product takes on, the method of processing it and the combination of these elements give origin to a wide range of typologies of Orosei Marble that can be ascribed to four main groups:

1. Veined (Fig. 1.6, a)
2. Cloud-like (Fig. 1.6, b)
3. Light (Fig. 1.6, c)
4. Pearled (Fig. 1.6, d)

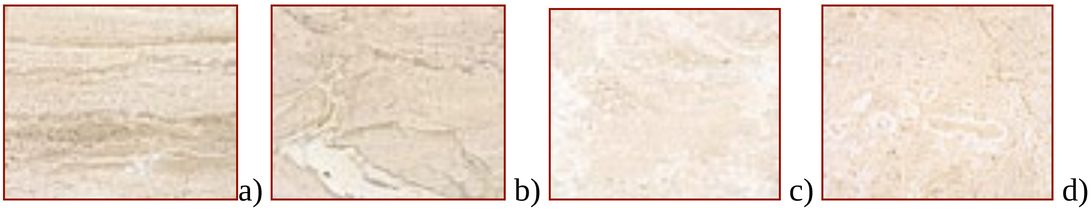

Figure 1.6: Main typologies of Orosei Marble.

Types of colouring

- Dark veined Orosei Marble
- Light veined Orosei Marble
- Dark cloud-like Orosei Marble
- Light cloud-like Orosei Marble
- Light Orosei Marble
- Pearled Orosei Marble

Processing methods

- Polished Orosei Marble
- Bushhammered
- Antique-like Orosei Marble
- Sanded Orosei Marble

1.1.5.3 Orosei Marble - Physical and mechanical characteristics

From microscopic studies previously conducted on samples of Orosei marble (Jurassic limestone) is showed that they are all composed of microcrystalline calcite and in particular (Siotto, G., 2006):

- The white type is made up of micrite (crypto and microcrystalline calcite) with interclasts (autochthonous fragments, resulting from the demolition of limestones by the waves) and bioclasts, also made by micrite with veins of microcrystalline calcite that sutured cracks of tectonic origin with an improvement of the mechanical properties of the material.
- The veined limestone consists of bioclastic grains, formed by foraminifers and by fragments of macro fossils and algae and interclasts of microcrystalline calcite in a micritic calcite mosaic, partly recrystallized.
- The *venatino* limestone, finally, consists of bioclasts foraminifers and by fragments of macro fossils in a mosaic of partially recrystallized micrite.

Orosei Marble is present on the market with chemical- physical and geo-mechanical features that change according to the type: *Orosei Marble*, *Veined*, *Light*, *Cloud-like* and *Pearled*.

This section contains the specifications relating to each of the seven firms and a card showing the average figures of Orosei Marble. They are the result of all the test reports from the individual businesses (marmidiorosei.it).

The specification cards highlight some typical features of the product, that are fundamental to identify specific connotations requested by the potential customers.

The figures are the result of a data processing carried out by *Centro Prove Materiali Lapidei Soc. Consortile arl*, after making all the necessary petrographic tests as required according to the regulations UNI EN 1341- 1342 –1343 in force since Oct. 2003.

Table 1.1: Values as indicated in EN 12524 rule.

<table>
<tr><td rowspan="4">TABLE FIGURES
ACCORDING TO EN 12524 REGULATION</td><td></td><td>Density</td><td>Determined thermal conductivity</td><td>Specific heat capacity</td><td colspan="3">Resistance factor to steam μ</td></tr>
<tr><td>Sedimentary rock</td><td>ρ= 2600 Kg/m3</td><td>λ = 2.3 W/(mK)j</td><td>Cp = 1000 J/(kg K)</td><td colspan="2">dry
250</td><td>wet
200</td></tr>
<tr><td></td><td>Density</td><td>Humidity content at 23°C</td><td>Humidity conversion coefficient</td><td colspan="2">Resistance factor to steam μ</td><td>Heat specific capacity</td></tr>
<tr><td>Processed stone items</td><td>ρ=1600-2400 Kg/m^3</td><td>50% RH
$\psi = 0,025\ m^3/m^3$</td><td>Fψ4</td><td>dry
150</td><td>wet
120</td><td>Cp = 1000 J/(kg K)</td></tr>
</table>

Table 1.2: Geo-mechanical characteristics of Orosei Marble.

OROSEI MARBLE PHYSICAL - MECHANICAL FEATURES (AVERAGE FIGURES)		
	Conformity with Regulation	
Petrographic description	EN 12407:2000	BIOPELSPARITE (Folk 1959, 1962)
Flexion resistance	EN 12372:1999	R_{tf} = 11.88 MPa
Flexion resistence after 48 freeze/de-freeze cycles	EN 12371:2001	R_{tf} = 10.36 MPa
Compression resistence	EN 1926:1999	R_m = 156 MPa
Compression resistence after 48 freeze/de-freeze cycles	EN 12371:2001	R_m = 151 MPa
Water absorption at atmospheric pressure	EN 13755:2001	0.5%
Apparent volume mass	EN 1936:1999	ρb = 2646 Kg/m^3
Open porosity	EN 1936:1999	p_o = 2.25%
Resistance to SO_2 activity under conditions of humidity	EN 13919:2002	A solution Δm = - 0.23 % B solution Δm = - 0.05 %
Water absorption through capillarity	EN 1925:2000	$C_2 = 0.67\ g/m^2s^{0.5}$

Thermic shock resistance	EN 14066:2002	Δm = - 0.01 %
	Conformity with regulation project	
Abrasion resistance	EN 14157:2001	18.02 mm

1.1.5.4 Orosei Marble - Uses

Since ancient times marble has been the most praised material due to its multi-use possibilities.

Italy is certainly the leading country detaining the best qualities and varieties of marble. The building of great public works accounts for its main uses; its applications are to be found in town streets and squares together with the linings of many palaces, seats of important office districts.

Orosei Marble is praised and widely used all over the world. It has been used in the building of the following: Gucci shops in Italy and all over the world; Charles De Gaulle airport in Paris and Santo Domingo airport; Lafayette Department Stores and the new underground in Paris; Singapore Golf Club; modern shopping centers in Zaragoza; the head office of the *Credito Industriale Sardo* in Cagliari, realized after a project by Renzo Piano.

As to residential housing and private building , marble finds employment in street furniture, linings of stairs and staircases, bathrooms, kitchens, interior and exterior pavings, fire-places and gardens.

The use of marble is goes from the sector of sacred and funerary art and to the field of artistic works, including the making of artistic mosaics, which has become more and more widespread during the last few years, due to a number of initiatives born with the aim of restoring artistic monuments in historic centers and in towns in general.

Finally, we would like to mention a sector which, even if considered less important for the small quantity of products employed, nevertheless brings prestige to Orosei Marble; we mean internal linings of large boats and private yachts together with artistic and architectural works of great value.

Another use is the one of the marble waste in the quarries and factories. Changed into grains and thanks to a high percentage of calcium carbonate (99% ca.), it makes excellent inerts for concrete and bitumen, to produce lime and cement. Moreover, it has some other interesting uses: it is used as a corrector of acid terrains in agriculture; to produce paper and glass, varnishes and polypropylene; in cosmetics and pharmaceutics; in the production of soda, fluxes for blast furnaces, neutralizers for acid industrial sewage, waterproof agents for dumps.

1.1.5.5 Orosei Marble - Businesses in the marble district

The Orosei Marble District numbers 16 businesses that run 15 quarries. The area has recently been classified by the Italian government as one of the four industrial districts in Sardinia, while the Autonomous Region of Sardinia (RAS) has acknowledged it as one of the four extractive areas of ornamental stones in the island (the other three regarding granite).

The Industrial District appears as a geographically concentrated community, made up of many technologically advanced small businesses, oriented to export; the exchange of goods, the transfer of technology and the commercial information implement a “business system” with a high competitive value.

Inside the district are extraction, transformation and product commercialization businesses. The firms are concentrated in adjoining areas and all of them are of small dimensions. Some businesses in the district – extracting and processing Orosei Marble – have seized an opportunity offered by SFIRS s.p.a. (= p.l.c.) and by RAS itself and thanks to the “Special Fund” - according to section 8 l.r. 37/98 - they have realized a project for the valorization of Orosei Marble.

The businesses in question are eight and account for – on their own – the entire extractive and working structure of Orosei Marble:

1. De.Da. s.r.l.
2. Gimarmi s.r.l.
3. Marmi Daino Real s.r.l.
4. Marmi Elmo di Gallus Antonio & C. s.a.s.

5. Mele Giovanni & Figli s.r.l.
6. S.I.M.G.$_1$ e S.I.M.G.$_2$ s.r.l.
7. S.Im.In. s.r.l.
8. Tirreno Marmi s.r.l.

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Link

www.marmidiorosei.it

2. WASTE AND REGULATORY FRAMEWORK

Wastes are objects, which the owner or holder wishes to dispose of or where their collection and treatment as waste is required by the public interest (OECD 1998, Modified).

In our time, there is a great concern among governmental agencies, contractors and environmentalist regarding the increasing amount of industrial waste throughout the world.

Nowadays, industries of all kinds are looking for alternative raw materials and have optimized their processes in order to reduce the amount of waste they produce and the corresponding environmental impact. In fact, is known that optimal solution for solid waste management is to minimize the amount of waste both at generation and disposal stage followed by preventive environmental management action.

2.1 Wastes From Stone Quarrying Activities

Stone industry is an important factor in worldwide economy. Despite this, a large amount of residues is produced in ornamental stone sector 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 (Marras et al., 2010).

One of the main environmental impacts of the ornamental stone extraction process is represented by the waste material that can reach a great quantity, even similar to the worked one. Wastes are usually stored in selected sites that should make a good use of the topography. Such sites should not offend the landscape, change the water regime or cause undesirable soil creepage (Osnet, Vol.12).

Quarrying is necessary to provide much of the materials used in traditional hard flooring, such as granite, limestone, marble, sandstone, slate and even just clay to make ceramic tiles.

Despite this, like many other man-made activities, quarrying involves the production of significant amounts of waste. Some types of quarries do not produce large amounts of permanent waste, such as sand and gravel quarries, whereas others will produce significant amounts of waste material such as clay and silt. The good news is that they are generally inert and non-hazardous, unlike the waste from many other processes. However, there is still potential for damage to the environment, mainly because of the treatment and disposal of the waste that may produce more negative impacts on the environment.

In order to extract the stone from the deposit an appropriate method of quarrying must be applied. The main objective of the exploitation method under the current strict framework of laws and directives concerning the environmental impacts should be the minimization of waste generation. The product of quarrying operations is the gangsaw block with dimensions about 1.5x1.4x2.8 m. During extraction large amounts of waste material are produced due to breakage of the products for various reasons such as physical–mechanical characteristics of the material, the degree of discontinuities in the deposit etc. The types of wastes generated from extraction activities of natural stones can be classified in four main categories based on their characteristics that condition the possibility of recovery (OSNET vol. 7, 2004):

a. Defective or “third choice” blocks with regular dimensions but either with poor technical-aesthetical properties or not the correct size for further processing.

b. Large shapeless blocks (= 0.2 m^3) which present excessive irregularity in geometry and cannot be sawed into slabs.

c. Small shapeless blocks (= 0.2 m^3 or dimension < 0.5 m) that are extracted from fractured parts of the deposit or derive from block squaring.

d. Small to fine size rocks (splints, chips) dust and slurry coming from drilling and cutting operations.

In all extraction activities the operations are carried out with water as a cooling agent for the equipment. Thus, amounts of slurry are produced which is a mixture of water and fine particles of the quarried material. In most cases slurry is collected and recycled in order to retrieve the water in the extraction process. The cake that remains contains about 20 - 30 % of water and is usually disposed in dumps.

Dimension stone cutting rejects (e.g. marble and granite) are inert and non-dangerous, but are becoming a worrying factor for industry owners and environmentalists alike. Waste can be used to produce new products or can be used as admixtures so that natural sources are used more efficiency and the environment is protected from waste deposits (Siddarth Pareek, 2001).

Quarry wastes are generated by mineral extraction and by the processing of minerals into saleable products. Most of these wastes are inert mineral materials which are disposed in stable above ground tips adjacent to the pithead or to the surface workings. These are then landscaped and restored. In 2001/2002 annual arising there were 110 million tones. About 5 million tones were recycled or re-used, mainly in the construction industry.

The smashing majority of the wastes produced in this industry is from prospecting and exploring the quarries, and from the posterior treatments of the extracted substances, namely wastes of prospecting and exploration of quarries, of used oils, of the packing, of the equipment out of use, and wastes of the commerce, industry and services, similar to the urban ones. These wastes are mostly deposited to the surface or in the subsoil, being very limited the efforts for its valuation.

In the European Waste Catalogue (EWC – Commission Decision 94/3/EEC) the code 01 00 00 is referred as "waste resulting from exploitation, mining, dressing and other further treatment of minerals and quarrying", with nineteen sub-codes.

The wastes produced directly in ornamental stone industries, can be considered as naturally occurring materials that must be removed to extract the stone or residues left after the processing of the stone, to produce saleable product. In the first case are included top soils, overburden and interburden stones (rock interbedded with the useful stone). In the second case, must be include blocks that does not have the proper dimensions or characteristics to be worked and fine grained materials derived from the beneficiation processes. Excluding top soil, all the others can be generally included in sub code 01 04 00 "waste from further physical and chemical processing of non-metaliferous minerals" as: waste gravel and crushed rocks, dusty and powdery waste, waste from stone cutting and sawing, wastes not otherwise specified.

The stone waste, although composed of the same material substances as the solid rock from which is derived, is not in the same physical condition because it was disaggregated, mixed and moved to a different place. The surface area will be increased by the reduction of particle size and consequent increase of volume.

The waste resulting from quarrying industry classified according to its potential for causing hazard to environment, can be considered most of the times as inert or non-hazardous and remains within the confines of the extraction operation. The essential difference between them is the size. The wastes could present very large particle size distribution, from blocks without the necessary characteristics for its recovery derived from the exploration itself, or small blocks which are the result of grinding and finishing processes, to particles of smaller sizes, with can achieve a few microns, in the form of mud resulting of cutting and polishing in the finishing operations.

Great volumes of stone waste with non appropriated dimensions are subsequently used to restore worked out sites, but during the quarrying waste it is necessary to accumulate them in large surfaces and in some cases, where the ratio of waste to material is high, it is not practical to return waste to the working quarry. This causes the accumulation in dumps of larger size, which is visually unappealing. (OSNET, Vol.12).

The fine-grained residues resulting from operations of cutting and polishing are usually stored in lagoons or dams where they settle out from process water which can be re-used. If they are not stored they can pollute the environment, both atmospherically and streams respectively if they are dry or wet. Another way to minimize this problem is the use of filters-presses that allow the preparation of solid material ready to be stored, with water content close to 20%.

2.2 Waste Management in Europe

Best practicable environmental option is to increase re-use or recycling.

The Waste Management aims at, preferentially, the prevention or reduction of the production of wastes or the reduction of their dangerousness. This is achieved namely through the reuse of materials and the alteration of the productive processes, adopting cleaner technologies, as well as through the sensitization of the economic agents and consumers.

Throughout Europe, it has come to be well-known an increasing concern and interest for the management of the industrial wastes, in form to be able to provide a harmonious development of a modern society through "sustainable" activities that promote the protection of the environment aiming at preferentially the prevention or reduction of the waste production, the adoption of cleaner technologies or the sensitization of the agents of the producers and the consumers, without affecting the social and industrial development.

The responsibility for the final destination of the residues is of who produces them, without damage of the responsibility of each one of the operators in the measure of its intervention in the circuit of management of these residues and except for what specific legislation determines. Therefore for the industrial wastes, the responsible are the enterprise that produces them. The costs of management of thes wastes must be supported by the respective producer. When the producer is unknown or indeterminate, the responsibility for the final destination to give to the residues and for the costs of the respective management fits to the respective detainee.

In what respects to the industrial wastes, all the producers or holders must also obligatorily have a register of the generated wastes and provide their correct treatment. Regarding the final destinations for the wastes, the legislation defines a hierarchy of preference to the possible destinations to give to the residues.

In this scope the following destinations are considered:

- Source Reduction.
- Recycling.
- Land filling / Elimination.

The existing European legislation approves the operations of elimination and valuation of the wastes, defining a specific code for each type of destination of the produced wastes, relatively to the operations of elimination.

Thus, the wastes must be eliminated without putting in danger the human health and without using processes or methods to attack the environment.

Also any operation of waste management, storage, abandonment, emission, transport, treatment, valuation or elimination of waste is subject to a previous authorization, except in the case of storage of industrial residues in the proper place of production.

The producer, the detainee and the transporters of wastes are responsible for the actual damages for the transport of residues, having the producer and the holder to assure that each transport, is made by companies permitted for its management.

The European Waste Catalogue aims to assure the identification and classification of wastes, as well as facilitating the perfect knowledge for the economic agents of the legal regimen they are related. This catalogue which came into force on the 1rst of January 2002 lists certain types of mining waste as hazardous. Wastes from the production of Dimensional Stone products may be characterized under several chapter headings, depending on the type of material, the production process, and the waste management techniques employed (European Council, 2001).

According to data of the European Community, the wastes of the extractive industry are about 30% of the residues produced annually in the European Union, corresponding to an annual volume of more than 400 million tons.

Manage these wastes in order to prevent or to minimize their adverse effect in the environment is the essential key for the correct functioning of the natural stone industry. But an adequate management of wastes implies a real knowledge as much in relation to its typology, the quantitative data generated in this activity, its characterization, final destiny, etc.

The waste management hierarchy is a concept that promotes waste avoidance ahead of recycling and disposal. The shortened version of the hierarchy “Reduce, Reuse, Recycle – 3R’s” is frequently used in community education campaigns and has become a well-recognised slogan for waste reduction and resource recovery (Gertsakis and Lewis, 2003).

The waste management hierarchy is a tool that policymakers have used to rank waste management options according to their environmental benefits. Policies based on the hierarchy seek to maximize the recovery options and to minimize disposal through open dumping and landfilling. Once possibilities for recovery have been exhausted, policies based on the hierarchy favor safe disposal, limiting negative impact on the environment and natural resources as much as possible.

The waste management hierarchy was ordered as follows (Pongrácz and 2004):

(a) Waste minimization

(b) Re-use

(c) Recycling

(d) Disposal

As a concept or principal, the hierarchy makes sense in a way that it is difficult to oppose. It echoes approaches that are widespread, i.e. prevention is better than cure. Most would agree that it is more effective to avoid problems from the outset, than to invest in reactive solutions once the problem has presented. As you can see, at the top of the hierarchy stands waste prevention as the most desirable option. After all, what has not been produced does not have to be dealt with.

2.3 Waste water purification system

As written before, in the sector of the natural rock, mainly in what respects to the activities of the extraction and transformation of the rock, in what refers to the process itself dangerous wastes are not originated. However, the type of processing lead to the production of great amounts of wastes, in particular, solids in the extraction and mud in the processing. These wastes will go to promote the occurrence of environmental impacts, besides being an incumbency for the companies.

Thus, part of the waste material deriving from stone production is a sludge, which can be controlled using settling tanks and holding lagoons. After drying and separation of the harmful materials, it is possible to obtain purified water and an inert waste that can be recycled for different purposes.

All the material used for this dissertation deriving from waste water purification systems belonging to the Orosei treatment plants.

The purification cycle process is described below (fig. 2.1):

a) The water from the cutting of marble is driven to the wastewater collection tank, which is made of concrete to our specifications. The tank collects all the water to be purified.

b) From the collection tank, the pump sends the water to the static decanters, whose capacity depends on the water flow/minute according to the hydraulic separation principle.

c) Along the way, the pipe lets in the “flocculant”, which is metered out according to the slurry contained in the water by the automatic metering system.

d) The water is pumped into the slurry decanters, the slurry precipitates under the effect of the flocculant to the bottom of the cone.

e) The purified water overflows into the well and falls back into the freshwater tank, perfectly clarified and ready to be reused in production.

f) The slurry settled in the decanters falls through the automatically-opening pneumatic valve (normally closed) into the steel tank below, to be homogenised.

g) As soon as the level probes are coated in slurry in the slurry tank, they send a signal to the centrifugal pump and the filtration cycle starts. The slurry is driven into the filter press, which in the meantime has closed the plate pack to form 30 to 50 mm chambers depending on the material to be filtered.

h) The slurry is fed into the filter press, where it is dehydrated up to 80% into compact panels, which can be perfectly stacked and which, when the filter opens, fall and pack up in the special containment walls or in the lorry bodies, ready for disposal.

i) For safety reasons, the clarified water recovered from the filter press is taken to the wastewater wells to be clarified all over again.

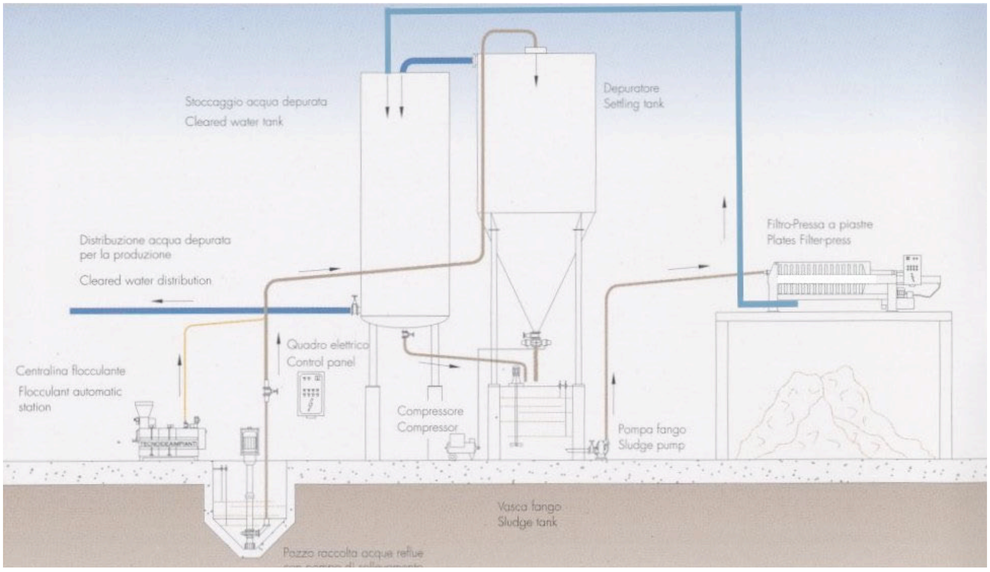

Figure 2.1: Waste-water treatment plant (modified from Tecnoidea Impianti).

2.4 Different Concepts of Waste

The notion of waste is relative in two main respects. First, something becomes waste when it loses its primary function for the user. A waste is therefore relative to this primary function. However, and this is the second perspective, what is considered waste with regard to this primary function may be useful for a secondary function (Bontoux and Leone, 1997).

This relative nature explains why certain wastes keep a significant economic value. While a waste may lose its value from who generated it, it may maintain a value for its secondary user who will be the one to set this value. The notion of waste is also relative to the technological state of the art and to the location of its generation.

One method of defining waste is by listing of activities or substances which come within the range of definition. An alternative method would be to define by reference to the purpose of the regulation. Most regulatory systems adopt a mixture of the two techniques (Poncrácz, 2002).

These simple notions may help shed some light on the current ongoing debates about European waste management. In its communication on the review of the European waste management strategy , the European Commission recognizes there is to date no satisfactory definition of when a product becomes waste nor of when a waste becomes a product again. It also recognizes that in spite of the intrinsic difficulty of the task, a serious effort from all actors is necessary to reach an adequate definition.

Many different concepts of waste exist in Europe. They have evolved in every Member States to respond to local geographical, cultural, historical and administrative conditions. As a result, the national concepts of waste vary from country to country and are sometimes difficult to translate.

The European framework directive on waste contributes to harmonize this situation but the European Commission complains that national laws still use definitions and classifications that depart from European terminology. The term “waste” has a negative image because it qualifies a material from the perspective of the upstream activity that generated it. It is the point of view of the person who cannot use it any more. However, it does not in any way mean that recovery or recycling is excluded. The French legislation introduced the additional notion of “ultimate waste” to describe waste for which no recovery is currently economically practicable.

2.5 Italian Regulatory Framework

The regulatory requirements governing the extractive industry and its products and waste are well-defined, both at the national and regional levels, especially as far as waste materials are concerned.

The basic regulation to be complied with is the Italian Legislative Decree No.152 of 3rd April 2006 concerning environmental matters.

Article 1 (a) of the EEC Directive 75/442 defines “waste” *as ‘any substance or object in the categories set out in Annex I which the holder discards or intends or is required to discard* (Decree 2nd May 2006, Ministry for the Environment and Land Protection).

The crux of the matter lies in this phrase. Ultrafine particles have up to now been considered as waste and treated as such by their producers. Actually there is a need to appreciate the potential value of this material and convert it into marketable products, thus doing away with the costs necessarily incurred by the extractive industry for its disposal.

Processing waste is classified under Italian regulations as special waste. These by-products are coded in the European Waste Catalogue as *010413* “*waste from stone cutting and sawing other than those mentioned under item 010407*”.

Article 186 of the Italian Legislative Decree No. 152, of 3rd April 2006, amended by D.Lgs. No.4 dated 16th January 2008, introduces changes for stone processing waste, exempting this material from the regulatory requirements for waste under particular conditions. More specifically, stone sawing and processing waste is not considered waste if it is utilized, without transformation, as envisaged in the project subjected to environmental impact assessment, or alternatively, approved by the competent authorities, when required, after endorsement by regional environmental protection agencies and as long as the material as a whole does not contain contaminants exceeding current regulatory limits.

The maximum permissible limits and analytic procedures for characterization of the constituents are established by a Ministry for the Environment decree. Until this decree is enacted the permissible limits established by Annex 1, col. B, of D.M. 471/99 will continue in force

From the above regulatory requirements it emerges that processing sludge can be converted into a marketable product.

2.6 Generated Waste in Sardinia

According to the “Report on Special Waste Management in Sardinia - Analysis of MUD 2005 data” published by the Environmental Protection Department of the Autonomous Region of Sardinia (April 2007), the stone industry generates 1,642,802 tonnes of waste each year in Sardinia.

This waste, classified as EWC 01, comprises 1,596,012 t/y of sludge. Practically the entire quantity of 1,640,241 t of non-hazardous waste generated by the stone industry in Sardinia are disposed of in waste dumps.

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 waste or slurry (Almeida et al., 2007).

In fact, the main difference in the waste generated during the production cycle in the quarry and in the stone processing facilities, lies in the size of the stone chips. Most of the coarser-size chips are processed in on-site crushers for size reduction and marketed as concrete and asphalt aggregates, for road bases and other uses. The finer size fractions including the sawing sludge are disposed of in the council waste site for inert materials.

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3. CALCIUM CARBONATE IN INDUSTRY

3.1 Generality

Calcium carbonate is a chemical compound with the chemical formula $CaCO_3$. It is a common substance found in rock in all parts of the world, and is the main component of shells of marine organisms, snails, pearls, and eggshells. Calcium carbonate is the active ingredient in agricultural lime. It is commonly used medicinally as a calcium supplement or as an antacid, but excessive consumption can be hazardous. It's also the most widely used filler. In the past its use was associated with a substantial cost reduction but today it is the material engineered for the different requirements of modern products (Handbook of fillers, 2007).

Calcium at 4.8% is the fifth most common elemental constituent of the earth's crust after oxygen, silicon, alluminium and iron. It's so popular in practical applications because it is found in rocks and minerals which have very high concentration of calcium carbonate. Calcium carbonate is the most common deposit formed in sedimentary rocks. There are three crystalline forms that are mostly used in production of calcium carbonate filler: trigonal - rhombohedral calcite, trigonal – scalenohedral calcite and orthorhombic aragonite (Bosshard of Omya/Plüss-Staufer AG).

Calcium carbonate filler has various industrial uses.

These include:

- Agricultural soil amendment;
- Manufacture of cement;
- 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;
- Flue gas desulphuration in electric power stations;

- Manufacture of lime, resin conglomerates for flooring and coatings in the building industry;
- A multitude of chemical applications, including cosmetics and pharmaceuticals.

Product specifications for the calcium carbonate vary depending on the application. In paper industry calcium carbonate is required for paper filling and paper coating, and it’s essential for a high press room performance, save ink, print quality, and commercialization of printed products at competitive prices.

In rubber production-line, ultrafine calcium carbonate adds strength without stiffness, acts as a pigment, and generates smooth extrusions (Industrial Minerals HandyBook, 2002).

The aim of the dissertation is to outline the study of potential application for marble dust as calcium carbonate in the perspective of reusing a waste products.

Ultrafine calcium carbonate dust recovered from marble sawing and processing slurries, have interesting applications or economically feasible industrial uses. This investigation aims to characterize and quantify the ultrafine calcareous particles in order to do a comparison with $CaCO_3$ industrial specifications (like paper, rubber and tires) and realize commercial products. In fact the high percentage of fines could well be recovered and marketed for a number of industrial applications that employ micronised calcium carbonate. Furthermore marble dust has various industrial uses, 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. By far the most effective and widely applicable option is to use the waste in civil and mining engineering works.

Several researches were carried out regarding different applications (Bertolini and Celsi, 1990); 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.

3.2 Industrial Uses

Since ancient times marble has been the most praised material due to its multi-use possibilities.

Italy is certainly the leading country detaining the best qualities and varieties of marble.

The building of great public works accounts for its main uses. Its applications are to be found in town streets and squares together with the linings of many palaces, seats of important office districts.

Orosei Marble is praised and widely used all over the world. It has been used in the building of the following: Gucci shops in Italy and all over the world; Charles De Gaulle airport in Paris and Santo Domingo airport; Lafayette Department Stores and the new underground in Paris; Singapore Golf Club; modern shopping centres in Saragoza; the head office of the Credito Industriale Sardo in Cagliari, realized after a project by Renzo Piano.

But currently, attempts are being made to utilize marble wastes in different applications like road construction, concrete and asphalt aggregates, cement, and other building materials, in particular the filter press mud (Dak, 2000) and so on. Some of the most interesting applications are listed below.

3.2.1 Brick making

The incorporation of various wastes in red clay-based ceramic products has been widely investigated, frequently with the aim of reducing the waste environmental impact (Saboya et al., 2007; Marras et al., 2010).

The use of marble sludge in the production of ceramics is an option for reuse, as studied in Chapter 6 of this dissertation.

Results have demonstrated that marble wastes can get better the problem of the expansion due to humidity in ceramic materials.

3.2.2 Mortars and Concrete

Technical possibilities of producing concretes containing marble dust have been reported in Chapter 6. Thus it can partially replace cement, pursuing the aim of minimize waste generation and disposal and also of producing revenue for companies.

3.2.3 Self Compacting Concrete

The self – compaction of fresh concrete is described as the ability of such concrete to fill up formwork and encapsulate reinforcing bars through the action of gravity alone, without any need for vibration and compaction, while maintaining adequate homogeneity.

The filler content in SCC plays important role. It provides not only flow ability to the concrete but also make concrete durable. If marble powder can be used as filler in self compacting concrete, problem of safe disposal will be reduced besides more durable concrete can be produced (Misra and Gupta, 2008).

3.2.4 Lightweight concrete

Use of marble powder for the production of lightweight concrete has been partially discussed in Chapter 8.

3.2.5 Clinker

Recent research studies concluded (Almeida et al., 2007; Aruntaş et al., 2010; Pereira et al., 2008) that there is technical viability to incorporate massive quantities of marble slurry as “raw material” in the production of clinker, without any previous complex treatments.

3.2.6 Paper Industry

Generally, calcium carbonate is used in the formulation of paints both as filler and as pigment.

$CaCO_3$ is used as a filler for making bright, opaque paper at minimum cost. Calcium carbonate also keeps the pH in the alkaline range (unless controlled with "acid-tolerant" technology).

In the production of paper from waste paper, the latter is mixed with water in a pulper that grinds it into a pulp. This pulp is then slowly purified by removing impurities depending on how thick the finished paper should be. Then, the cleaned and purified pulp is ground more and put in a mixer with fillers, pigments and more water. The mixture is very thin and poured into a net, on which the paper begins to be produced. After that, the net is passed through various presses, which remove more water, while the last drying operation involves passing it through hot cylinders which dry out the paper with steam. Then, the dry product passes through a polishing device which presses it before rolling it up: the paper is now ready to be converted into different types of paper.

Calcium carbonate is added to the mixture at the very beginning along with fillers and pigments, and is added again during the polishing stage, when the paper must become suitable to take ink. Depending on the type of paper, the percentage of calcium carbonate added as filler ranges between 4 % and 10 %, and similar amounts are added during the polishing operation. It must be noted that kaolin and talc can also be used as fillers, but calcium carbonate has become increasingly important recently, since kaolin (which used to be commonly used as a pigment) is much more expensive to extract and transport than calcium carbonate. Paper products using calcium carbonate as a pigment are: paper and cardboard for graphic applications, paper rolls for newspapers, writing and printing paper, white cardboard and board white packaging paper and cardboard. Please note, however, that calcium carbonate somehow wears out the paper nets (depending on its rhombohedral crystallization) even if not all carbonates are equally abrasive. To reduce abrasion, the $CaCO_3$ should have 60 % of its particles under 2 microns, resulting in 50 % to 90 % of the particles used being under 2 microns. The particle size of the limestone is carefully checked since particles larger than 60 microns would cause great problems when mixed: at least 50 % of the limestone used usually has a particle size of less than 2 microns. In addition, the filler should contain low amounts of silica, aluminium silicate, iron oxide, iron sulphur, etc. since such particles damage the net and alter the colour (white) of the finished products. Even if the composition of the filler is usually 98% calcium carbonate, 1% humidity and 1 % impurities, such as silicates and other minerals, an extender containing more than 90 % $CaCO_3$ is considered acceptable provided iron, lead and other ore contents are low enough not to alter the white colour of the product, which is essential for water paints.

In paper industry the use of the calcareous marble sludge involves a preliminary selection of the colour (Paragraph 3.3.1), particle size and purity of the sludge. They should therefore be ground beforehand to produce particle sizes that are 100 % smaller than 50 microns and at least 60-90 % smaller than 2 microns. In addition, they should contain high amounts of $CaCO_3$ (at least 95 %), low amounts of silica, and they should be evenly white and contain no metal dust or impurities that could alter the colour of the finished paper. Humidity should not be a problem since the finished product is sold as slurry. In conclusion, white marble sludge seems perfectly suitable for the purpose, once they have been adequately ground and sifted.

3.2.7 Plastic fillers

3.2.7.1 Polypropylene (PP)

Polypropylene is a thermoplastic material with a high softening temperature and good elasticity and mechanical resistance. During production, PP is mixed with varying amounts of inert fillers, normally of mineral origin, each one affecting the resistance of the finished product.

Calcium carbonate is used as filler only for rigid and less resistant materials, such as interior decoration, packaging etc.

The properties and calcium carbonate content used in PP with a comparatively low mechanical resistance depend on the finished product for which they are intended. The $CaCO_3$ used to produce packaging films must have a very small particle size (less than 2 microns) and a filler percentage of 30-40 %, while that used to produce packages can have slightly larger particles (under 10 microns) and a filler percentage up to about 60 %.

Calcareous sludge could be used in this sector provided that their properties are adjusted to decrease humidity to no more than 0.1 % of their weight. Magnesium would cause no problems, while the iron content should be very low to avoid oxidative catalytic processes, especially in the PP used to produce packaging films or when appearance is of concern (white), but it would be less important in the production of rougher materials (crates). In any case, particle size may be a problem since it could be reduced by grinding and sifting.

3.2.7.2 Polyvinyl chloride (PVC)

Polyvinyl chloride is a very common thermoplastic resin used mainly in two forms: rigid or flexible.

$CaCO_3$ is largely used as a filler to produce PVC, not to provide the filled material with any special property, but just to save on the cost of the raw materials and because it has a better tolerance to impurities than PP. Once again, the particle size depends on the finished product, although its upper limit remains 40 microns. Particle sizes of less than 2 microns must be 20 % for belt or strip PVC and between 50 % and 90 % for wire insulators.

Sludge made of marble alone seems to have the right formulation, while its particle size must be reduced to optimum values just like its humidity content that must not exceed approximately 0.1 %. Special treatments are therefore required, such as grinding and forced drying. Remarkable amounts can be used, since PVC can be filled with remarkable amounts of inert materials (as much as 60 %).

3.2.8 Soil stabilization

Some work has also been undertaken to improve the properties of soils by addition of marble dust.

Calcium by-products are largely used to correct the acidity of excessively acidic farmlands. In particular, acidic soils have a pH of 3-3.5, while alkaline ones have a pH of 9-10. Acidity depends on the presence of peat soils rich in humus acids or on the rainwater leaching the soil for a long time. Normally, correction involves soils with an acidity level equal to a pH of 4.5 since lower pH values would require different crops (Barral et al., 2005).

One can easily argue that calcium carbonate is much slower in reducing acidity than other correcting agents (CaO, $Ca(OH)_2$). The amounts to be used depend on the acidity level and on the crop.

There are restrictions, of course, on the content of heavy metals, which must be equal to or lower than that allowed for farming fertilizers. Sludge could therefore be directly used without having to be filter pressed or ground into chips. Sludge could perhaps also be used as “a slurry” (i.e. containing high amounts of water) and directly poured onto the soil. There are problems, however, with the competition of other correcting agents, which have a quicker reaction time, and with transport since there are not many acidic soils in Italy and shipping these agents to other countries would be simply too expensive.

3.2.9 Production of fertilizers

Calcium nitrate $Ca(NO_3)_2$ is commonly used as a fertilizer (Davini, 1998) in farming as a source of calcium and nitrogen and is usually made by direct reaction between a solution of nitric acid and solid calcium carbonate, as follows:

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + CO_2 + H_2O$$

To speed up this heterogeneous reaction, the contact between the reagents should be facilitated, so the calcium carbonate (which is generally made of adequately ground quarry limestone) should have a fairly low, particle size. It could therefore be profitably replaced with marble sludge.

The particle size of these sludge seems to be fine enough (under 300 microns) for the intended use, and the humidity content of filter pressed materials should not cause any problem since the above reaction takes place in the aqueous state (but the use of thinner materials is not recommended, not to dilute the nitric acid solution too much). The usual problem remains, i.e. the high metal content that should not exceed the limits imposed on fertilizers, and transport. The latter seems to be the more restrictive one.

3.2.10 Flue gas desulphurization from thermoelectric plants

Sulphuric acid is very harmful both to health and to environment. It causes remarkable environmental damage even from a distance. We should consider that, in the open air, all marble work is transformed from calcium carbonate into calcium sulphate which crumbles easily and hence destroys the work over time. To control these problems, strict law regulations have been enforced, limiting the amount of SOx that can be let out during combustion. Such pollutants are reduced by using fuels with a low sulphur content but it is economically unfeasible to reduce such content to less than a given percentage, so the waste gases produced by combustion are adequately submitted to the so-called fume desulphurization process. The "desulphurizer" used in this case is pure CaCO3 or $CaCO_3$ transformed into CaO or calcined and then hydrated into $Ca(OH)_2$ (Fraes, 1994; De Bresser et al., 2005). The SO_x reducing processes can then be either “dry” or “wet”.

In dry processes, the calcareous dust comes into contact with the SOx through injection into the fume manifold at a high temperature. To remove satisfactory amounts of both SO2 and SO3, CaO should be injected, which, under the effect of heat, turn into a variant of CaO showing a large surface area and is therefore highly reactive. Overall, the reaction is as follows:

$CaO + SO_2 + \frac{1}{2} O_2 = CaSO_4$

If a solid fuel such as coal is used, the desulphurization of waste gases simply starts in the combustion chamber where coal is burnt in fluid bed systems after having being mixed with limestone. In this process, CaCO3 is calcined into CaO which then reacts with SO_2 and O_2, thus forming calcium sulphate (as described above) with a reduction of more than 90% with coal containing approximately 1 % sulphur.

In “wet processes”, combustion fumes come into contact, in special absorption towers, with an aqueous suspension of lime or limestone. Such processes have a high efficiency, removing over 95% SOx and using a high amount of reagents, but they cause problems with the cooling of the gases (to approximately 55°C) and with the load losses caused by the “scrubbing” process. In addition, other problems are related to the production of high amounts of calcium sulphate sludge (plus combustion ashes). In particular, a number of “wet” plants have been built that use suspensions of calcareous materials (that, for the sake of brevity, we will not describe in detail), but in any case the disposal of large amounts of calcium sulphate, which, because of the low cost of the pure material, cannot always be sold as gypseous material, is something of a problem.

"Wet processes" utilize a $CaCO_3$ suspension, and so the humidity level of the sludge is not a problem. But they must contain high amounts of $CaCO_3$ (90-95 %). Impurities are not a problem, but iron by-products can act as catalysts in the subsequent oxidation of sulphite into sulphate. Their particle size should however be checked to obtain stable suspensions of calcareous materials. The consumption of calcareous sludge that could be used in this industry seems promising in terms of amounts and because no selection is required between pure white marble and slightly coloured marble.

3.3 Comparison with Industrial Specifications

Diverse applications have different quality requirements (Industrial Minerals HandyBook, 2002), and for many of these uses, price, availability, particle size, purity and colour are of paramount importance (Careddu et al., 2009; Siotto et al., 2008).

The marble sludge deriving from the Orosei treatment plants was submitted to a characterization in order to evaluate the compatibility with the industrial specifications required by particular sectors.

For this comparison was utilized the mud deriving from the SIMG plants.

3.3.1 Paper

Currently, three different classes of minerals are used for paper filling and paper coating: kaolin, talcum and calcium carbonate. Their functional properties are multiple (Naydowski, 1999), $CaCO_3$ in paper is essential for a high press room performance, save ink, print quality, and commercialization of printed products at competitive prices. In particular the difference in brightness of this raw materials have led to a dynamic growth in the uses of $CaCO_3$ for paper manufacturing around the globe.

Table 3.1: Characteristics required to $CaCO_3$, in paper manufacturing, compared with sampled muds.

Parameter	**Value**	**$SIMG_1$ sludge**	**$SIMG_2$ sludge**
$CaCO_3$ [%]	95 - 98	96.5	95.2
Average particles size [µm]	< 3	3.9	5.2

3.3.2 Rubber

In rubber production-line, ultrafine calcium carbonate adds strength without stiffness, acts as a pigment, and generates smooth extrusions (Industrial Minerals HandyBook, 2002).

The table lists some of the characteristics required to $CaCO_3$ compared with sampled muds.

Table 3.2: Chemical and physical characteristics required to $CaCO_3$, in rubber manufacturing, compared with sampled muds.

Parameter	**Value**	**SIMG1 sludge**	**SIMG2 sludge**
Chemicals			
$CaCO_3$ [%]	98.5	96.5	95.2
SiO_2 [%]	0.1- 0.4	0.43	0.70
Fe_2O_3 [%]	0.08	0.05	0.10
Physical			
Specific Weight [g/cm^3]	2.70	2.72	2.69
Particles size <10.5 µm [%]	82 - 90	77	65

3.3.3 Production of tires

For similar reasons seen in the case of rubber production, calcium carbonate is also utilized in the production of compounds for tires construction.

Table 3.3: Chemical and physical characteristics required to $CaCO_3$, in tires manufacturing, compared with sampled muds

Parameter	**Value**	**SIMG1 sludge**	**SIMG2 sludge**
Appearance	**White to light grey powder**	**White**	**White**
Fineness			
-150 µm	100 %	99 %	100 %
-45 µm	> 95 %	63 %	55 %
$CaCO_3$	> 92 %	96.5 %	95.2 %
Cu	< 0.005 %	0.0056 %	0.0039 %
Mn	< 0.05 %	0.0036 %	0.0056 %

It should be noted that the greater proportion of Cu in the $SIMG_1$ mud, compared to $SIMG_2$ one, is no doubt attributable to the contribution of the metal linked to the consumption of sawblades segments utilized during the block cutting process.

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4. CALCIUM CARBONATE DUST CHARACTERIZATION

4.1 Introduction

Marble sludge was supplied by the five companies mentioned in the thesis introduction, which operate limestone quarries and stone cutting facilities in the area. These enterprises are members of the Orosei Marble district. The plants are equipped with both block cutters, milling cutters and also with a sludge water purification system.

As written before, this dissertation is finalized to study the effect of addition of marble powder on the properties of marketable products. Therefore, in order to characterize the marble dust were carried out physical, mineralogical and chemical determinations.

Basically, the importance of this chapter is to characterize exactly the "waste" that we must apply for further applications. Conventionally, the original purpose of waste characterization was to determine if a waste needs to be managed as a hazardous waste and that a major secondary purpose was to evaluate a treated waste to determine if it could be removed from regulation as a hazardous waste.

However, all the dehydrated sludge used in the dissertation was previously analyzed.

4.2 Materials and methods

As mentioned, marble sludge was supplied by the plants belonging to the Orosei Marble District, in the waste-water treatment plants and in particular at the exits of the filter press sections as you can see in figure 4.1.

Was followed the circuit of waste water and collected samples at each point of interest:

1. directly in the treatment plant;
2. wastewater collection tank;
3. over - settling tank;
4. under - settling tank;
5. filter-press.

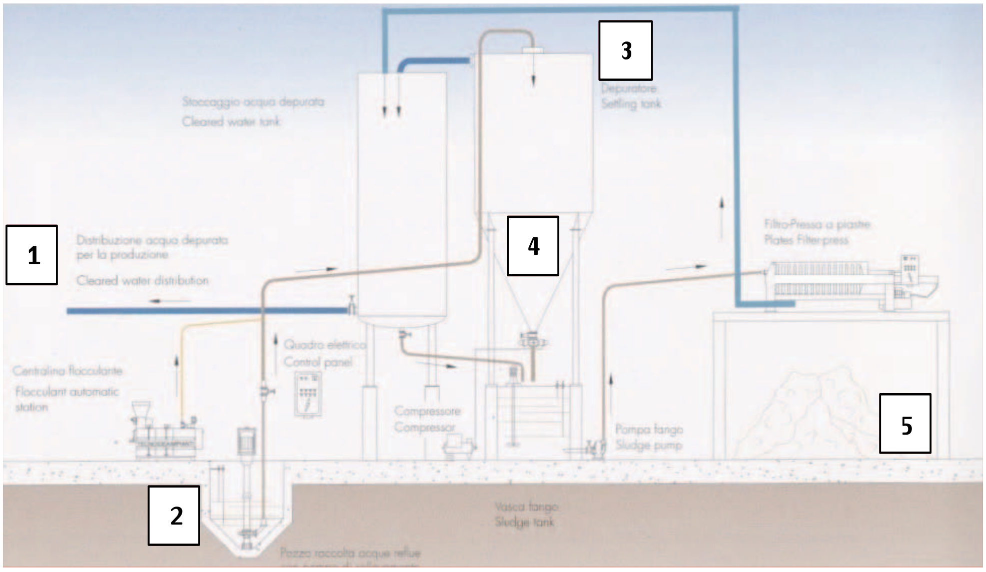


Figure 4.1: Sampling points (modified by Tecnoidea Impianti).

After the sampling stage *in situ*, it was moved at the characterization out and out. Firstly, to verify the basic condition of reutilization, the leaching tests were carried out and secondly physical, chemical and mineralogical analyses. The entire framework of the analyses carried out in the characterization program are listed below:

1. Leaching test;
2. Grain size distribution;
3. Bulk density measurement;
4. Mineralogical determination;
5. Chemical analysis with the technique of the lithium metaborate fusion and ICP-AES;
6. Loss on ignition;
7. SEM determination;
8. Colorimetry and bright analysis.

Marble sludge powder was obtained in wet, containing about 25 - 30% moisture, form directly taken from deposits of marble factories. The collected samples of slurry were put in an oven to dry at a temperature of 110 ± 5 °C. At fixed intervals (1 hour, 4 hours, 12 hours, 24 hours, 48 hours, and 72 hours) the weight loss was registered with the aim to reach the constant weight. Since most of the samples were semi liquid, they have be very gradually dried until they were transferred to a ventilated oven with thermostat to control the temperature.

Before starting the analysis phase, reduction by quartering was made, in order to obtain the representative samples to a convenient size for testing. The followed principle is that the quarter should be representative of the whole. The correct sampling and sample preparation of material are imperative if reliable analytical results are expected.

For one hand, samples deriving directly from plants, from over and under of the settling tanks were semi-liquid so they were agitated for homogenising the slurries and not allowed the sedimentation at the bottom of the cans, used in sampling, and afterwards quickly toppled in liquid divider. Ideally, it is important to include the solids in the sample and to limit its accumulation during the application of the method. These steps were repeated for each semi-liquid samples until arriving at on-quarters of can.

For the other hand, samples deriving from the filter press sections were straight dried in the oven until constant weights were reached and subsequently reduced in quantity by *splittering*. The splittering of the sample has the purpose to divide the sample into two equal portions and it is performed by an instrument called “Splitter”. The sample splitter, called also “riffle”, consists of alternate sections that form chutes which drop the sample portion alternately to one side or another. The divided sample is caught in two collection pans placed at each side of the equipment. If the sample is still too large for analysis needs, the splittering protocol is repeated until to reach the desired amount.

By this methods, representative samples of marble dust were extracted. Five representative samples of filter - press sludge was prepared so as to determine the moisture content, using the control weight method and the values are reported in Table 4.1 and all the values obtained are in line with the literature.

Table 4.1: Moisture values.

SAMPLE	**MOISTURE [%]**
$SIMG_1$	27.09
$SIMG_2$	22.34
SIMIN	24.96
DeDa	24.41
DAINO REAL	25.33

4.2.1 Leaching tests

The material object of the experimentation, because they are waste production processes, have been previously characterized by leaching test. In this way it has been possible to verify the compliance with the limits prescribed by the regulations on waste and in particular the Italian Legislative Decree No.281 of 1st December 2010. The reference values are shown in Table 4.2 “Concentration limits of the eluates for the acceptability at landfills for inert waste”.

Analytical samples were prepared for submitting them at the leaching tests. The procedures to prepare the solutions is the one indicated in the UNI 10802, for manual sampling and preparation and analysis of eluates.

The method was made by performing the compliance leaching test EN 12457-2 test on the untreated marble sludge. The method consisted of mixing 10 g of powder in 100 ml of distillate water (L/S= 10) for 24 h. After filtration at 0.45 µm, the metals concentrations in the solution were measured with ICP-OES spectrometry (Varian, 710 ES).

The analysis was carried out according to the articles 8 and 9 of the Italian Legislative Decree No. 186/ 2006.

Table 4.2: Concentration limits (Modified by Table 2 D.M. No. 281/2010).

Parameter	**L/S=10 1/kg** [mg/l]
As	0.05
Ba	2
Cd	0.004
Cr_{total}	0.05
C	0.2
Hg	0.001
Mo	0.05
Ni	0.04
Pb	0.05
Sb	0.006
Se	0.01
Zn	0.4
Chlorides	80
Fluorides	1
Sulfates	100
Phenol Index	0.1
DOC	50
TDS	400

4.2.2 Grain size distribution and bulk density

The fine-grained fraction of a sediment is defined as silt (particles with diameters less than 62 microns down to 4 microns). Because of their small size, fine-fraction particles are difficult to measure by sieving. For this reason, grain size analysis was conducted on the dry solid cakes produced by the filter-press using a *Sedigraph 5100 Analyser,* instrument using X-Ray absorption (Vitton and Sadler, 1994).

In addition, 100 g of representative samples, respectively of $SIMG_1$ and $SIMG_2$, were carried out for sieve grain size analysis in order to divide dust into fractions. Tyler sieve size was used, under 100 microns: 75, 53, 38, 20, 10, 5 [μm]. For the 10 μm and 5 μm sieves were extracted 10 g of samples and the analysis was conduct with the help of an ultrasonic device.

The portions of marble dust deriving from the laboratory analysis were prepared with the technique of the fusion metaborate fusion, and checked with an inductively coupled plasma atomic emission spectrometer (ICP-AES manufactured by Varian), for verifying if the use of flocculant, in the waste water treatments plants, or the use of abrasive, in the polishing phase, could pollute the slurry.

Table 4.3: Sieve analysis (Tyler size).

FRACTION	**$SIMG_1$ [g]**	**$SIMG_2$ [g]**
+ 75 µm	0.8	4.6
(- 75 + 53) µm	0.5	2.6
(- 53 + 38) µm	2.6	8.3
(- 38 + 20) µm	5.1	7.6
- 20 µm	91	76.9
TOTAL	**100**	**100**
(- 20 + 10) µm	1.5	1.8
(- 10 + 5) µm	0.9	3.1
- 5 µm	7.6	5.1
TOTAL	**10**	**10**

Bulk density of representative samples of the filter pressed materials in the processing plant was determined using an Accu Pyc 1330 gas pycnometer manufactured by Micromeritics Instruments.

4.2.3 Mineralogical analyses - X-Ray diffraction

The crystalline minerals present in the solid residue were identified using X-ray powder diffraction analysis. The XRD scan was conducted on the dewatered slurries to determine mineralogical composition. The diffractometric analyses were performed using a RIGAKU device with Cu-Ka radiation (copper tube operated at 30 kV and 30 mA).

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

4.2.4 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 using a plastic stirring. 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 millilitres 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.

Marble dust samples, deriving from all the five plants above mentioned, were studied and also the fractions obtained from sieve analysis (cf. Paragraph 4.2.2 and Table 4.3) and the TENAX abrasives (tenax.it).

The marble dust fractions and the abrasive solutions were examined by inductively coupled plasma atomic emission spectrometry (ICP-AES) manufactured by Varian (Varian 710 - ES). On the other hand, marble dust sample ICP-AES measurements were made by Actlabs-Activation Laboratory – Ontario, Canada (actlabs.com).

4.2.5 Loss on ignition

The loss on ignition (LOI) 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).

LOI measurements were made both by Actlabs - Activation Laboratory (Ontario - Canada) and DiGITA Laboratory (University of Cagliari).

4.2.6 SEM determination

Scanning electron microscope was used in the laboratory of Higher Technical School of Mining Engineering - Technical University of Madrid. A marble dust sample deriving from the treatment plant belonging to DeDa company was submitted to SEM-determination.

4.2.7 Colorimetry and bright analysis

Cf. Paragraph 4.4.

4.3 Results and discussion

4.3.1 Leaching tests

The following table shows the results of the leaching tests compared with the limit values.

Table 4.4: Leaching test results and comparison with the limit value [mg/l] according to the Annex 3 Legislative Decree No. 186/2006.

PARAMETER	LIMIT	SIMG$_1$	SIMG$_2$	SIMIN	DEDA	DAINO REAL
SO_4^{2-}	250	11.76	< 10	< 10	< 10	19.54
CN^-	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Cu	0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Zn	3	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

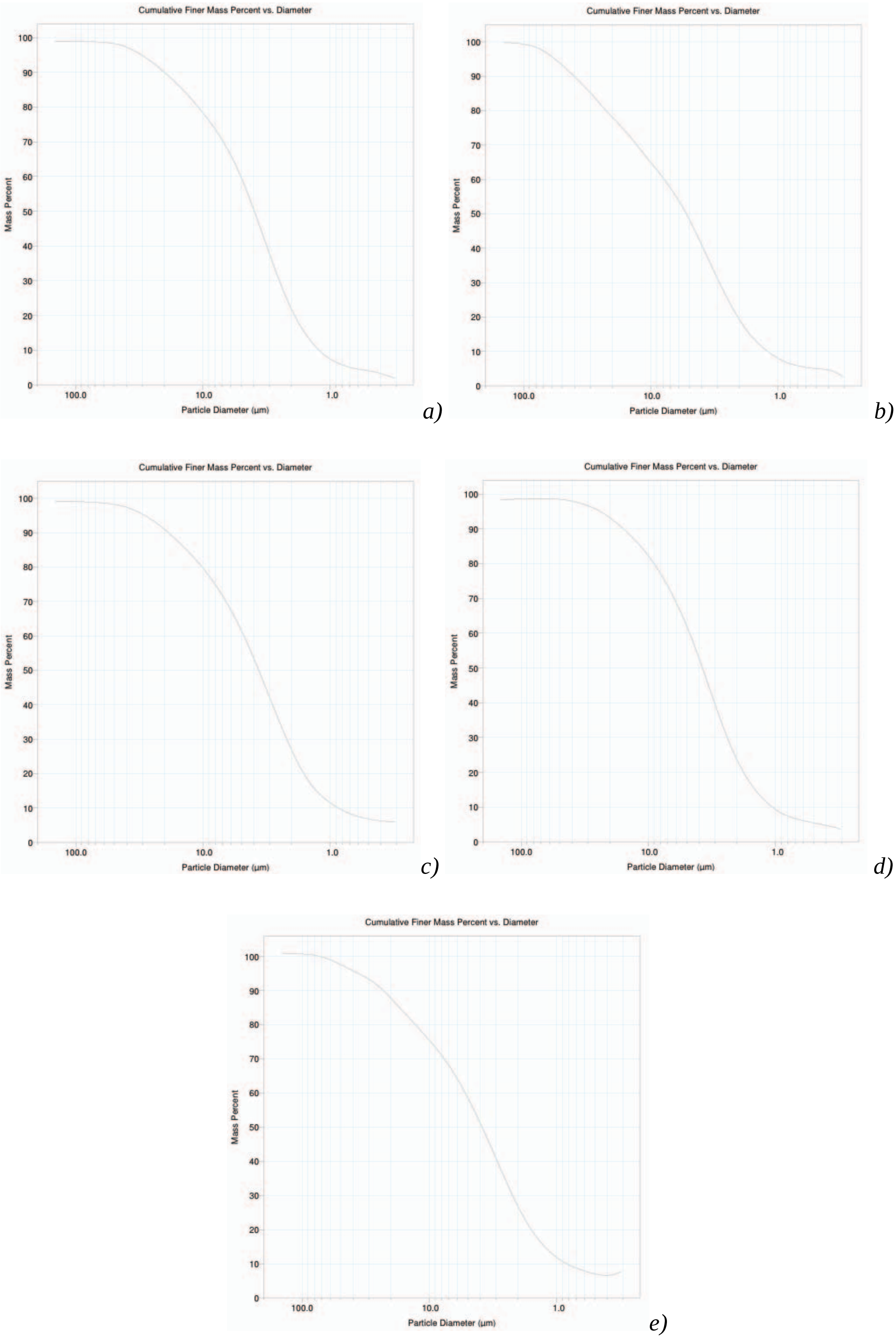
Ni	0.01	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
As	0.05	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Cd	0.005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Cr $_{tot}$	0.05	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	0.05	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Se	0.01	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Hg	0.001	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
pH	5.5 < > 12	9.48	9.52	9.63	9.50	9.57

All waste parameters were measured in the eluates, whose concentrations are below the limit specified in the table in Annex 3 to Decree No. 186, 2006, and may be subject to simplified procedures for recovery and reuse in accordance with Italian regulations (Italian Legislative Decree No.152/2006). In addition, these residues are classified as inert as it does not exceed the concentration limits for the acceptability of in landfills for inert waste (Table 2 in Decree No. 281, 2010).

Furthermore, the analytical results obtained here confirm that this type of waste not needs to be managed as a hazardous waste and there is no constrains in adding marble dust for making by-products.

4.3.2 Grain size distribution and bulk density measurement

The grain size distributions for the representative samples were reported in Figure 4.2 a, b, c, d and e. Test conditions are detailed in Appendix 1.A-B-C-D-E, lists of the readings, statistic reports, and the curves “Mass frequency vs Diameter”.



a) b) c) d) e)

Figure 4.2: Grain size distribution. a) SIMG$_1$; b) SIMG$_2$; c) SIMIN; d) De.Da.; e) Daino Real.

It’s important to note that calcium carbonate dust characterization showed that the particles are very fine, as resulted in the grain size curves, of the order of the micrometer. The main fraction of the material exhibits grain sizes of below 25 μm.

Bulk densities plant were determined and transcript below.

Table 4.5: Bulk density determinations.

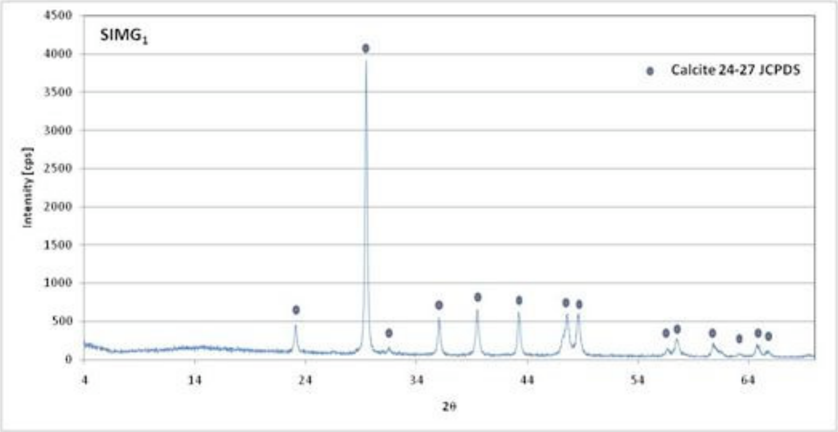
SAMPLE	**Bulk Density [g/cm^3]**
SIMG$_1$	2.72
SIMG$_2$	2.69
SIMIN	2.66
DeDa	2.77
DAINO REAL	2.69

The bulk density is the typical density value for marble.

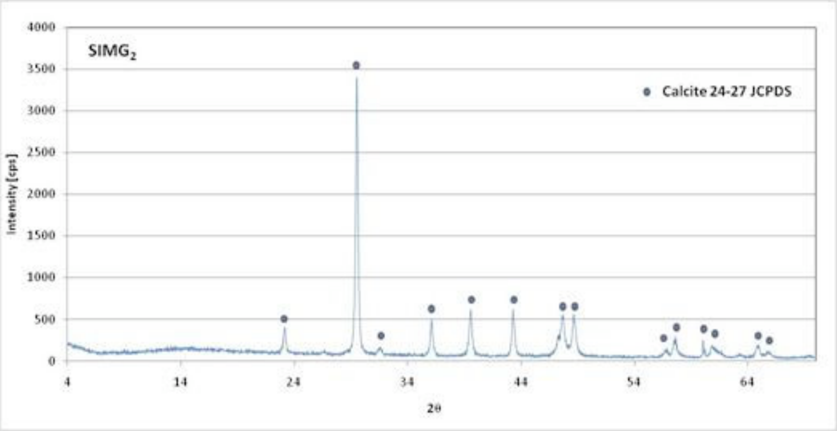
4.3.3 Mineralogical determinations

Determinations are carried out for identifying the marble powder mineralogical composition. The XRD analysis was performed on the dewatered slurries.

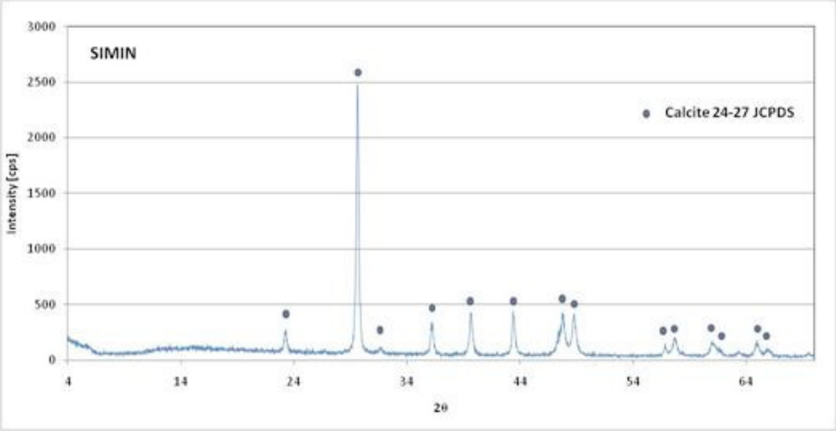
As is demonstrated in the following figures, the XRD spectra for all the sludge is the only mineral constituent detected, determined by comparison with the JCPDS index, 24-27 JCPDS.



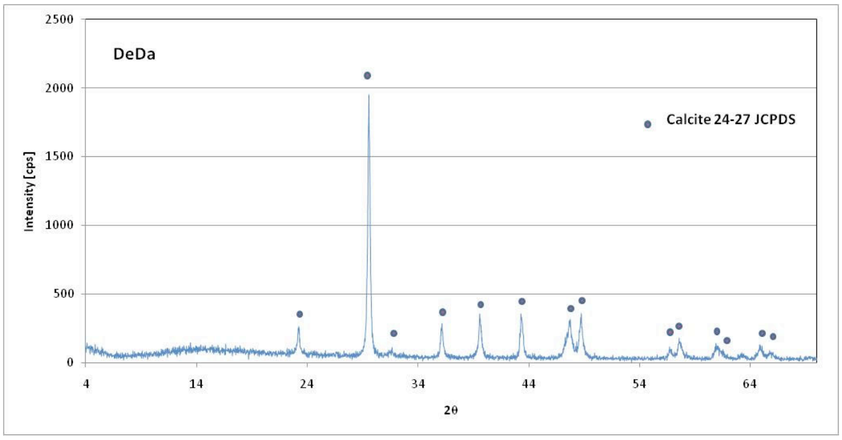
a)


SIMG$_2$
● Calcite 24-27 JCPDS
Intensity [cps]
0
500
1000
1500
2000
2500
3000
3500
4000
4
14
24
34
44
54
64
2θ

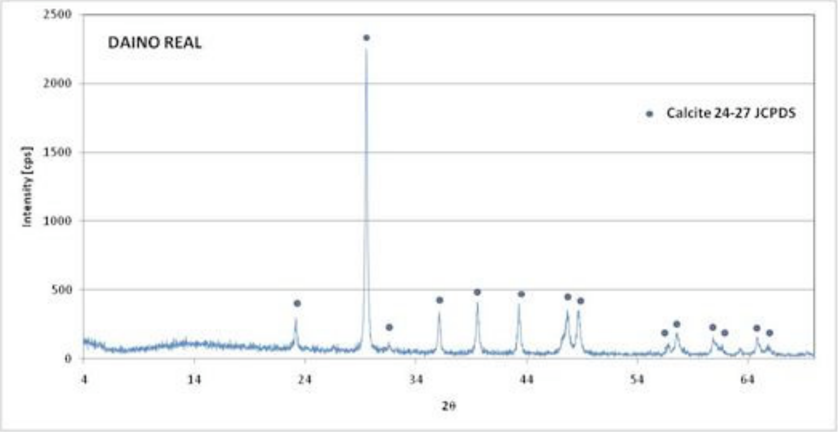
b)


SIMIN
● Calcite 24-27 JCPDS
Intensity [cps]
0
500
1000
1500
2000
2500
3000
4
14
24
34
44
54
64
2θ

c)


DeDa
● Calcite 24-27 JCPDS
Intensity [cps]
0
500
1000
1500
2000
2500
4
14
24
34
44
54
64
2θ

d)



e)

Figure 4.3:Mineralogical spectra.

4.3.4 Chemical analyses and loss on ignition

The data of chemical compositions and relative proportions in oxides and trace elements are indicated in Table 4.6.

Table 4.6: Actlabs data.

ANALYTE SYMBOL	**UNIT SYMBOL**	**DETECTION LIMIT**	**SIMG$_1$**	**SIMG$_2$**	**DAINO REAL**	**SIMIN**	**DEDA**
SiO_2	%	0.01	0.08	0.6	< 0.01	< 0.01	0.01
Al_2O_3	%	0.01	0.08	0.28	0.07	0.04	0.07
$Fe_2O_{3(T)}$	%	0.01	0.04	0.12	0.03	0.03	0.03
MnO	%	0.001	0.005	0.009	0.005	0.007	0.004
MgO	%	0.01	0.46	0.52	0.44	0.47	0.43
CaO	%	0.01	54.9	53.47	52.59	54.04	54.22
Na_2O	%	0.01	0.02	0.03	0.02	0.02	0.02
K_2O	%	0.01	< 0.01	0.04	< 0.01	< 0.01	< 0.01
TiO_2	%	0.001	0.005	0.014	0.003	0.002	0.003
P_2O_5	%	0.01	0.02	0.08	0.03	0.03	0.03
LOI	%	____	43.82	43.86	45.13	43.94	43.9
Total	%	0.01	99.46	99.02	98.33	98.56	98.72
Sc	ppm	1	< 1	< 1	< 1	< 1	< 1
Be	ppm	1	< 1	< 1	< 1	< 1	< 1
V	ppm	5	< 5	< 5	< 5	< 5	< 5

Cr	ppm	20	< 20	< 20	< 20	< 20	< 20
Co	ppm	1	< 1	< 1	< 1	< 1	< 1
Ni	ppm	20	< 20	< 20	< 20	< 20	< 20
Cu	ppm	10	< 10	< 10	< 10	< 10	< 10
Zn	ppm	30	< 30	< 30	< 30	< 30	< 30
Ga	ppm	1	< 1	< 1	< 1	< 1	< 1
Ge	ppm	1	< 1	< 1	< 1	< 1	< 1
As	ppm	5	< 5	< 5	< 5	< 5	< 5
Rb	ppm	2	< 2	< 2	< 2	< 2	< 2
Sr	ppm	2	161	177	165	159	153
Y	ppm	2	< 2	< 2	< 2	< 2	< 2
Zr	ppm	4	30	11	5	< 4	7
Nb	ppm	1	< 1	< 1	< 1	< 1	< 1
Mo	ppm	2	< 2	< 2	< 2	< 2	< 2
Ag	ppm	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
In	ppm	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Sn	ppm	1	< 1	< 1	< 1	< 1	< 1
Sb	ppm	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Cs	ppm	0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Ba	ppm	3	13	17	4	4	7
La	ppm	0.1	1.2	1	0.3	0.3	0.4
Ce	ppm	0.1	1.9	1.5	0.3	0.2	0.4
Pr	ppm	0.05	0.18	0.18	< 0.05	< 0.05	0.06
Nd	ppm	0.1	0.6	0.7	0.1	0.1	0.2
Sm	ppm	0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1
Eu	ppm	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Gd	ppm	0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1
Tb	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Dy	ppm	0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1
Ho	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Er	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Tm	ppm	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Yb	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Lu	ppm	0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
Hf	ppm	0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2

Ta	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
W	ppm	1	< 1	< 1	< 1	< 1	< 1
Tl	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pb	ppm	5	< 5	< 5	< 5	< 5	< 5
Bi	ppm	0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Th	ppm	0.1	< 0.1	0.3	< 0.1	< 0.1	< 0.1
U	ppm	0.1	0.2	0.4	0.3	0.2	< 0.1

The ICP-AES data for the $SIMG_1$ and $SIMG_2$ fractions are detailed in Appendix 2.C, moreover the abrasives utilized in treatment plants were analysed, with the same method, and the results were reported in Appendix 3.A. As confirmed by the test data, the abrasive abrasives have not polluted sludge.

LOI data were calculated as average value of the different measurement carried out by Actlab Laboratory and DiGITA laboratory.

Table 4.7: LOI determinations.

SAMPLE	**Loss on Ignition [%]**
$SIMG_1$	43.82
$SIMG_2$	43.86
SIMIN	43.94
DeDa	43.90
DAINO REAL	45.13

The marble waste dust contains very minor amounts of impurities, and the values obtained for the loss on ignition demonstrate that the analyzed samples have high content of CaO consequently is clear that the original stones are nearly pure carbonate.

4.3.5 SEM Determination

Marble dust characterization showed that the particles have micrometer size and it can be observed that the marble sludge powder had a high specific surface area (Figure 4.4). This could mean that is addition should confer more cohesiveness to specific building materials.

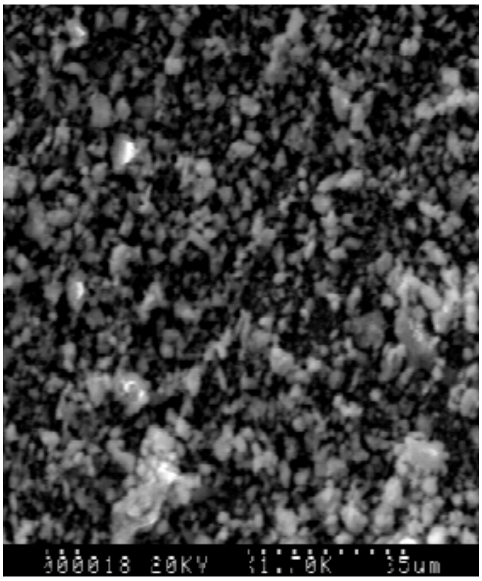


Figure 4.4: DeDa marble powder SEM-photo (80x)

4.4 Colorimetry and Brightness Analysis

Among the merchandising parameters required to carbonate powder, for some application field (especially paper) there are also the chromatic characteristics. Therefore the measurements for colorimetry and brightness determination were carried out on all the samples taken from the filter presses.

4.4.1 Equipment

Photoelectric Reflectance Photometer ELREPHO produced by Carl Zeiss S.p.A. (courtesy of C.N.R. – I.G.A.G.) was used during the study. It is shown in Figure 4.5a.

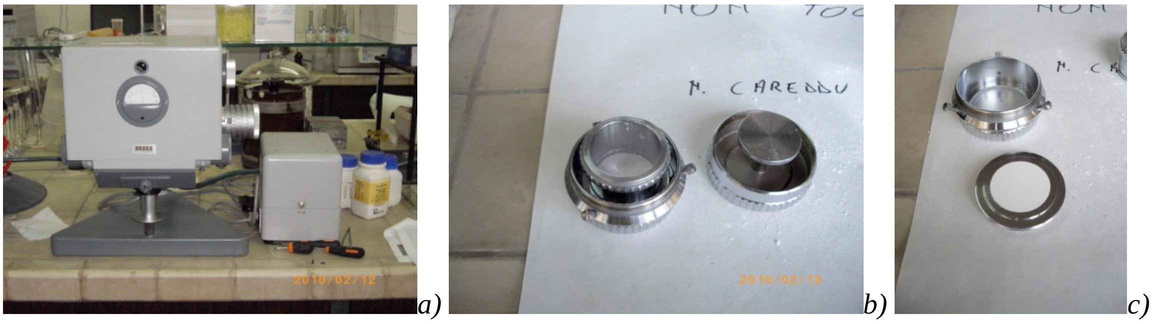
According to the Commission Internationale de l’Enclairage (CIE) standards, the light source used was the illuminating agent “C”. It is an approximation of the light of a cloudy sky. To obtain this kind of illuminating agent from the incandescent lamp, which is equipped with the device, a set of light filters has to be used.

Filter R 457 is mainly used for measuring the directional reflectance in the blue spectral range (brightness) of pulp and paper. The effective wavelength of 457 nm has the very close tolerance of ± 0.5 nm.

The effective wavelengths of R-filters (R 57, R 53 and R 49) are dispersed approximately uniformly over the visible spectral range so that the spectral pattern of the directional reflectance of a test sample is approximated if measurements are made with all R-type filters. Such a complete measurement will always be valuable when slight color differences of samples have to be determined. This applies in any case to typical patterns of the samples to be compared. For routine sampling, measurement may be restricted to the use of those one of two filters with which the greatest differences have been found.

Tristimulus filters are used to determine the tristimulus values in the CIE system. The photometer used in this study has the following filter set: FMX/C, FMY/C and FMZ/C. These filters are used to determine the tristimulus values for illuminant C.

Powder of every single sample was used to fill the powder press (Figure 4.5b) for forming the sample dish (Figure 4.5c).



a) b) c)

Figure 4.5: a) *Photoelectric Reflectance Photometer ELREPHO; b) Sample dish mould; c) Powder sample dish.*

4.4.2 Measurements

According to his function, Barium sulphate powder was used as primary reflectance standards for calibration of the secondary standard.

Data are listed in Table 4.8.

Table 4.8. Directional reflectance for all the powders. Calibration values are given in relative for barium sulphate.

POSITION OF FILTER CHANGER	**FILTER DESIGNATION**	**DIRECTIONAL REFLECTANCE**					**LAMPS, VOLTAGE [V]**
		SIMG$_1$	**SIMG$_2$**	**DAINO REAL**	**SIMIN**	**DeDa**	
1	R 68						12
2	RI 62						
3	R 57	90.48	87.70	90.28	90.80	92.65	
4	R 53	88.92	85.35	88.80	89.38	91.30	
5	R 49	86.85	82.30	87.34	88.25	90.35	
6	R 46						
7	R 42						
8	R 457	84.57	79.22	84.16	84.88	87.13	
9	FM X/C	90.63	87.85	90.46	90.98	92.75	
10	FM Y/C	89.35	86.00	89.15	89.78	91.65	
11	FM Z/C	87.53	79.20	84.09	84.80	87.10	
12	no filter						

4.4.3 Brightness

R-filters and the R 457 one were used primarily to complete the investigation. However, the measurements obtained were not subsequently used.

Interestingly, the powder produced by DeDa is found to have a higher brightness than the others. On the contrary, the SIMG$_2$ 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 same company.

4.4.4 Colorimetry

The surveys were carried out according to what was fixed by the Standard of the Italian Unification Office (UNI) 8941: coloured surfaces – Colorimetry. The standard regulation provides the methods for instrumental determination of the three-chromatic coordinates and of the differences in colour of coloured surfaces.

Considering the possible coordinate systems, the present regulation recommends the use of the following systems:

- CIE 1931 colorimetric system
- CIE 1964 colorimetric system

The colorimetric functions in both systems cannot be converted into one another, because the two systems have different physiological bases.

As previously mentioned, insofar as the distances in the colorimetric spaces of the two aforesaid systems are not proportional to the differences of visual perception in the whole space, it is advisable to use the three-chromatic coordinates of the CIELAB colorimetric space (also called CIE 1976 L* a* b*, shown in Figure 4.6) that result more uniform than the two previous ones and that are calculated with the appropriate formulas.

The processing of the results, summarized in Table 4.9, shows a high tendency towards white (expecially for the DeDa powders), strategic parameter for the paper industry.

There is also a tendency towards yellow especially in the $SIMG_2$ product due to what has been explained above.

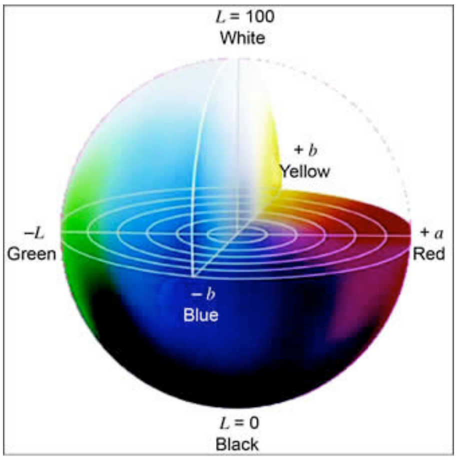


Figure 4.6: CIE Lab colour space (Modified from Oleari C., 1998).

Table 4.9. Directional reflectance for all the powders. Calibration values are given in relative for barium sulphate.

	$SIGM_1$		$SIGM_2$		DAINO REAL		SIMIN		DeDa	
	CIE 1931	**CIE 1964**	**CIE 1931**	**CIE 1964**	**CIE 1931**	**CIE 1964**	**CIE 1931**	**CIE 1964**	**CIE 1931**	**CIE 1964**
L*	95.73	95.73	94.31	94.31	95.64	95.64	95.90	95.90	96.68	96.68
a*	5.45	6.90	6.51	7.94	5.50	6.95	5.30	6.75	5.11	6.57
b*	11.70	10.62	15.19	14.15	13.96	12.90	13.90	12.84	13.63	12.56

4.5 Conclusions

According to this characterization, the calcium carbonate sludge deriving from the Orosei treatments plants sludge consist of calcium carbonate, substantially pure. Marble dust was tested to identify the absence of pollutants, thus confirming that it could be used in commercial applications. Through chemical analysis has showed that chemical elements, such as Si, Ti, Fe, alkali and heavy metals are present in very low concentrations compared to those found in similar material from different Italian regions. These very fine particles present chemical and nature similar to pure calcium carbonate.

These factors ensure that the sludge production can have a potentially high economic value, and also for their very fine particle size it can be used in new production cycles.

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alla Gazzetta Ufficiale Italiana n. 114 del 18 maggio 2006). And subsequent amendments.

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Links

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5. CONCRETE

5.1. Generality

Concrete is used more than any other man-made material in the world. Generally concrete is used to make pavements, pipe, architectural structures, foundations, motorways/roads, bridges/overpasses, parking structures, brick/block walls and footings for gates, fences and poles. It is for these reasons that a further investigation of the reuse of marble dust in concrete production appeared to be warranted.

The word concrete comes from the Latin word "concretus" (meaning compact or condensed), the past participle of "concresco", from "con-" (together) and "cresco" (to grow).

Concrete is a mixture of cement, sand (fine aggregate), small stone or gravel (coarse aggregate) and water and other cementitious materials such as fly ash and slag cement, and chemical admixtures. Commonly cement used is the Portland one, and generally the aggregates are distinguished in coarse aggregates, that are made of gravels or crushed rocks such as limestone, or granite, and fine aggregates such as sand. Through a chemical reaction called hydration, the paste hardens and gains strength to form the rock-like mass known as concrete.

There are many types of concrete available, created by varying the proportions of the main ingredients. By varying the proportions of materials, or by substitution for the cemetitious and aggregate phases, the finished product can be tailored to its application with varying strength, density, or chemical and thermal resistance properties.

Recently, the use of recycled materials as concrete ingredients has gained popularity because of increasingly stringent environmental legislation. The most conspicuous of these is fly ash, a by-product of coal-fired power plants (Scott, A. N., Thomas, M.D.A., 2007; Halstead, W., 1986). This significantly reduces the amount of quarrying and landfill space required, and, as it acts as a cement replacement, reduces the amount of cement required.

Different studies were carried out in order to evaluate the feasibility of substituting aggregates with ornamental stone waste (Almeida et al., 2006; Almeida et al., 2007; Binici et al., 2007; Chitlange et al., 2008; Coriandolesi et al., 2010; Güneyisi et al., 2008; Misra and Gupta, 2008) and also of replacing cement with marble powder (Topçu et al., 2008; Alyamaç and Ince, 2008) but for mortars not for concrete.

Limestone and dolomite fines are the most frequently used to increase the content of fine particles in self compacting concretes among non-pozzolanic fillers (Binici et al.,2007; Billberg, 1999).

In this chapter we have tried to demonstrate the possibility of this final solution.

5.2 Materials

For this study the mixed materials were derived from the combination of four components and water: cement (CEM), coarse aggregates (CA), fine aggregates (FA) and marble dust (MD). Firstly, were carried out physical, mineralogical and chemical determinations in order to characterize the marble dust. Secondly, concrete specimens were prepared in the LOEMCO laboratory (Madrid – Spain) by mixing of the components with marble powder in different proportions.

Now we describe each single component in details.

5.2.1 Cement

Cement is crushed limestone, blended with other raw materials (sometimes shale and or sand) ground into a powder and then heated in a kiln. This process produces a cement clinker which is mixed with gypsum and ground further to produce the cement.

About 1.6 billion metric tons of cement is sold each year (cemex.it). Cement as basic and irreplaceable building material has wide usage, its world production has reached almost 1.500 million tons (Rosković, R. et al.). Because of its many favorable qualities, builders worldwide use our cement for almost every kind of construction project.

Cement's many qualities (strength, durability, and flexibility, among others) make it the world's most popular building material. Especially, cement is hydraulic because, when mixed with water, it chemically reacts until it hardens. Cement is capable of hardening in dry and humid conditions, and even under water.

Portland cement is the most common type of cement in general usage (conforming to UNI EN 197-1).

Type I 52.5 R cement (52.5 Grade) was used in the laboratory program, with the physical and chemical properties tabulated in Table 5.1.

Table 5.1: Physical and chemical properties of CEM I 52.5 R.

No.	Property	Value
1	Specific density	3.13 g/cm^3
2	Specific surface area	5,040 cm^2/g
3	Initial Setting time	115 min
4	Final Setting time	165 min
5	Strength 2 days	39 MPa
6	Strength 7 days	51 MPa
7	Strength 28 days	61 MPa
8	Loss on ignition (LOI)	2.45%
9	Insoluble Residues (IR)	0.68%
10	Sulfates	3.18%
11	Chlorides	0.016%
12	Expansion	0.5 mm

5.2.2 Aggregates

The crushed stone, sand, and gravel are used in virtually all forms of construction. Aggregates are not only a key component in the construction and maintenance of highways, roads, and streets, but also an indispensable ingredient in concrete.

Fine and coarse aggregates make up the bulk of a concrete mixture. Sand, natural gravel and crushed stone are mainly used for this purpose. Recycled aggregates (from construction, demolition and excavation waste) are increasingly used as partial replacements of natural aggregates, while a number of manufactured aggregates, including air-cooled blast furnace slag and bottom ash are also permitted (Ahmed, I., 1993).

Accounting for 60% to 70% of the total volume of concrete, aggregates strongly influence concrete's freshly mixed and hardened qualities. They not only increase concrete’s strength, but also can make the mix more compact, enabling applications such as weatherproofing and heat retention. They can further contribute to concrete’s aesthetic qualities. For example, sand gives surface treatments their brightness.

Aggregates were supplied by CEMEX (Spain). In Spain, CEMEX is the cement leader industry (cemex.com). It’s one of the world's largest suppliers of aggregates: primarily the crushed stone, sand, and gravel used in virtually all forms of construction. Its aggregates are obtained from sand-and-gravel pits, hard-rock quarries, or by dredging marine deposits.

Two different types were used in this research: fine and coarse aggregates.

5.2.2.1 Fine aggregates

Fine aggregate is the sand used in mortars. FA utilized in this study have the following characteristics: 5 mm maximum size, with 0.7% passing the 63 μm sieve was used (Figure 5.1).

Figure 5.1: Fine aggregates used in the experimentation.

Its relative density (at saturated surface dry condition SSD) was 2.59, and its SSD condition water absorption of < 0.5%. The sieve analysis of the fine aggregate is presented in Table 5.2 and was conducted according the UNI EN 933-1: 2009 and the UNI EN 933-2: 1997.

Table 5.2: Grain size analysis FA.

Sieve size [mm]	**Retained [%]**	**Passing [%]**
4	6.3	93.7
2	27.9	72.1
1	55.6	44.4
0.5	82	18.0
0.25	94.1	5.9
0.125	98.2	1.8
0.063	99.3	0.7

Table 5.3: Physical properties of FA.

Fineness modulus [%]	3.0
Specific gravity [g/cm^3]	2.59 ± 0.04
Water absorption [%]	< 0.5

Fineness modulus is only a numerical index of fineness, giving some idea of the mean size of the particle s in the entire body of the aggregate. To a certain extent it is a method of standardization of the grading of the aggregate. It is obtained by adding the percentage weight of material retained in each of the standard sieves and dividing it by 100.

5.2.2.2 Coarse aggregates

CA have the following characteristics: 20 mm maximum size, with < 0.5% passing the 63 μm sieve was used (Figure 5.2).

Figure 5.2: Coarse aggregates used in the experimentation.

Its relative density was 2.61, and its water absorption of 0.5%. The sieve analysis of the fine aggregate is presented in Table 6.4 and was conducted according the UNI EN 933-1: 2009 and the UNI EN 933-2: 1997.

Table 5.4: Grain size analysis CA.

Sieve size [mm]	**Retained [%]**	**Passing [%]**
40	0.0	0.0
31.5	0.0	0.0
20	1.2	98.8
14	48.2	51.8
12.5	71.2	28.8
10	96.3	3.7
8	96.3	3.7
5	99.7	0.3
< 0.063	< 0.5%	___

Table 5.5: Physical properties of CA.

Fineness modulus [%]	1.2
Specific gravity [g/cm^3]	2.61 ± 0.02
Water absorption [%]	0.5 ± 0.1

The coarse aggregate unless mixed with fine aggregate serves no purpose in cement works.

5.2.3 Water

A tap water available in the concrete laboratory was used in manufacturing the concrete, the public water was supplied by the aqueduct of Madrid (Isabel II).The qualities of water samples are uniform and potable.

Combining water with a cementitious material forms a cement paste by the process of hydration. The cement paste glues the aggregate together, fills voids within it, and allows it to flow more freely.

Less water in the cement paste yields a stronger, more durable concrete; more water gives a freer-flowing concrete with a higher slump. Impure water used to make concrete can give problems when setting or causing premature failure of the structure.

Hydration involves many different reactions, often occurring at the same time. As the reactions proceed, the products of the cement hydration process gradually bond together the individual sand and gravel particles, and other components of the concrete, to form a solid mass.

Reaction:

Cement chemist notation: $C_3S + H \rightarrow C\text{-}S\text{-}H + CH$

Standard notation: $Ca_3SiO_5 + H_2O \rightarrow (CaO)\bullet(SiO_2)\bullet(H_2O)(gel) + Ca(OH)_2$

Balanced: $2Ca_3SiO_5 + 7H_2O \rightarrow 3(CaO)\bullet2(SiO_2)\bullet4(H_2O)(gel) + 3Ca(OH)_2$

So, water is a very important part of the mix and the volume of water used can dictate the strength of the finished mix. On site a "slump test" was used to test the water content of the concrete.

5.2.4 Marble Dust

Cf. Chapter 4.

5.3. Experimental Phase

The *mix design* depends on the type of structure being built, how the concrete will be mixed and delivered, and how it will be placed to form this structure. Mixing concrete correctly is vital for durable and long lasting foundations, to create a proper concrete mix.

The character of the concrete is determined by quality of the paste. The strength of the paste, in turn, depends on the ratio of water to cement. The water-cement ratio is the weight of the mixing water divided by the weight of the cement. High-quality concrete is produced by lowering the water-cement ratio as much as possible without sacrificing the workability of fresh concrete. Generally, using less water it produces a higher quality concrete provided the concrete is properly placed, consolidated, and cured.

Concrete solidifies and hardens after mixing with water and placement due to a chemical process known as hydration, as written before. The water reacts with the cement, which bonds the other components together, eventually creating a stone-like material.

The theoretical calculation of the dosage must always be added with an experimental test to verify that the requirements were satisfied, if these were not achieved would proceed to correct the dosage or, if necessary, to change methods.

This project was concentrated on a general purpose mix.

5.3.1 Slump test

The properties of fresh concrete were measured according to UNI EN 12350-2:2009. A cone made of steel was used for this test and the ingredients were thoroughly mixed in mixer machine till uniform consistency was achieved.

The fresh concrete is compacted into a mould in the shape of a frustum of a cone. The cone is 300 mm high, with a top opening of 100 mm diameter and a bottom opening of 200 mm diameter.

The materials used were moistened to prevent loss of water from the mixture, and reduce friction between the paste and mould. The cone was filled in three phases and a bar was used to compact the concrete and remove air voids, within the cone, picking 25 times.

Filling the cone, it went over the mouth of it with the trowel. The cone was then lifted vertically, as quickly as possible. The amount by which the concrete drops below the mold height is measured and this represents the slump. By laying the bar on top of the cone, it was be possible to measure how far the concrete "slumps", that provides a measure of the consistency of the concrete.

Table 5.6: Slump test values [cm].

	Mix-design I	**Mix-design II**
CMI_0	4.9	5.0
CMI_5	4.5	4.7
CMI_10	4.4	4.5
CMI_15	4.0	4.2

5.3.2 Mixing Concrete

Concrete mixes were designed by assuming a good degree of quality control and moderate exposure conditions. The mixes are designed for CMI_0 CMI_5 CMI_10 CMI_15 CMII_0 CMII_5 CMII_10 CMII_15.

For the first calculated mix design we studied several scientific researches and applied the same procedure and the same proportions (Güneyisi, E., et al., 2008).

For the second one was used the ACI method (Fernández, M. 2007). The American Concrete Institute (ACI) mix design method is one of many basic concrete mix design methods available today.

This method is based on choosing a minimum strength for test-concrete (Fernández, 2007), fixing a value of strength, the water - cement ratio is associated with this strength.

For the study was chosen a strength value of 30 MPa and the associated water-cement ratio of 0.55, and for a finesses modulus of 2.7 was employed the equation whose graph is shown below (Figure 5.3) to calculate the coarse aggregates volume to be used in mix-design, and the value obtained was 0.63 for every 10^{-3} concrete volume (Fernández, 2007).

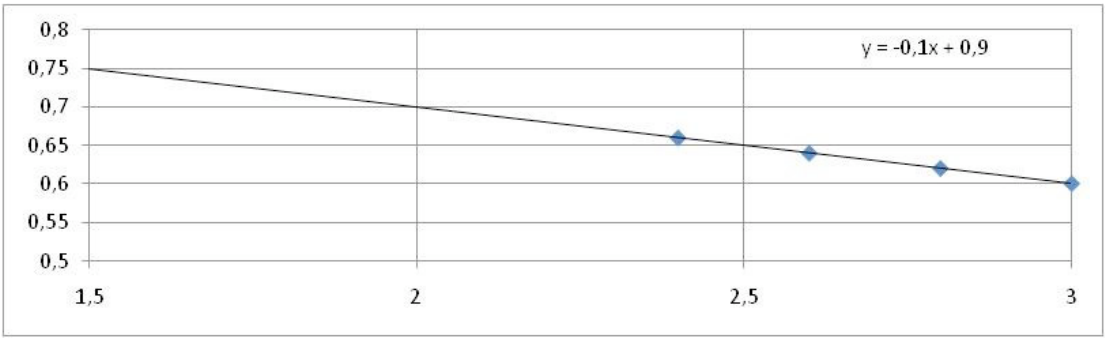


Figure 5.3: Straight line for calculate coarse aggregates volume (Fernández, 2007).

Summarizing the figures obtained are reported in Table 5.5.

Table 5.7: Mix-design II data

Maximum size for coarse aggregates [mm]	20
Strength at 28 days [MPa]	30
Water / cement ratio	0.55
Slump [cm]	3 a 5
Water absorption [l/m^3]	185
Finesses modulus [%]	2.7
Specimen volume [cm^3]	5,301.45

The source data are listed in the table below.

Table 5.8: Physical properties of the components.

Material	Bulk density [kg/dm^3]	Specific weight [kg]
Cement	3.1	1.12
Water	1	1
Coarse aggregates	2.65	1.57
Fine aggregates	2.65	1.57

The dosage per cubic meter is shown in the following table (Table 5.9)

Table 5.9: Mixture per cubic meter calculated by ACI method.

Material	Volume [dm^3]	Mass [kg/m^3]	[%]
Cement	108.50	336.36	13.70
Water	185.00	185.00	7.54
Coarse agregates	373.25	989.10	40.30
Fine aggregates	356.25	944.06	38.46

Recapitulating, two different mix-designs were calculated to cover the range of different mixture variations, and a total of 4 concrete mixtures for each mix-design, were proportioned having a constant water-binder (cement and marble dust) ratio (Güneyisi et al., 2008).

The control concretes for both the mix-designs were made without incorporating marble dust.

Thus, test specimens were prepared in the LOEMCO laboratory by direct mixing cement (CEM), coarse aggregates (CA), fine aggregates (FA) adding marble dust (MD) in different proportion (by weight) and water (Figure 5.4). Cement being mixed with sand and water to form concrete. The exact amount of concrete ingredients were weighed and mixed together. The workability of fresh concrete was measured in terms of slump

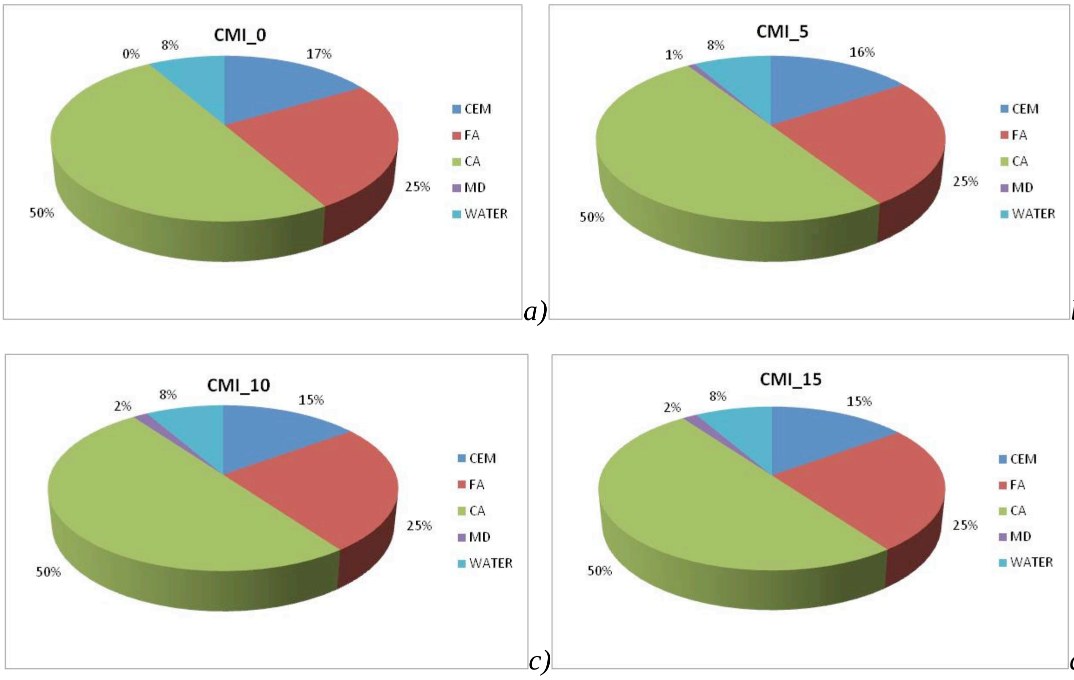
(Paragraph 5.3.1). Cement was replaced with waste sludge at various percentages by weight (0%; 5%; 10%; 15%) to prepare the concrete mixtures, fixing water to CEM+MD ratio at value of 0.5 (by weight) for the first mix design and 0.55 for the second one.

Figure 5.4: Concrete components ready to be mixed.

All the values are tabulated in Table 5.8 and graphically represented in Figures 5.5 and 5.6.

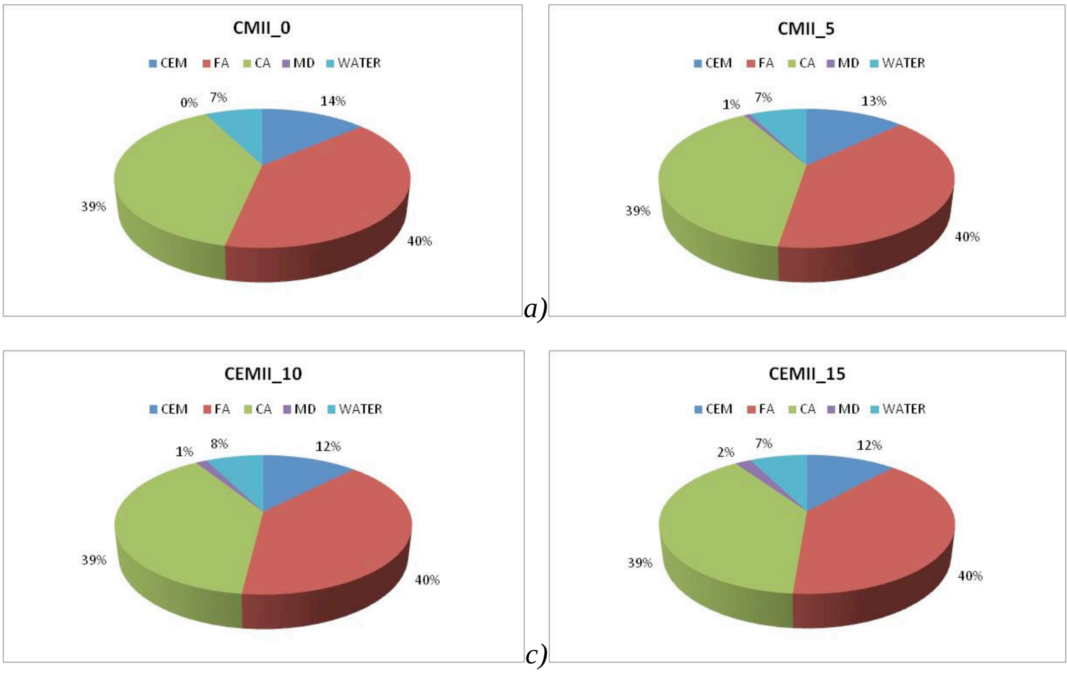
Table 5.10: Mixture proportions of the two mix-designs [kg]

<table>
<tr><th colspan="7">MIX-DESIGN I</th></tr>
<tr><th></th><th>W/(CEM+MD)</th><th>CEM</th><th>FA</th><th>CA</th><th>MD</th><th>WATER</th></tr>
<tr><td>CMI_0</td><td>0.5</td><td>8.3</td><td>12.5</td><td>25</td><td>0</td><td>4.2</td></tr>
<tr><td>CMI_5</td><td>0.5</td><td>7.9</td><td>12.5</td><td>25</td><td>0.4</td><td>4.2</td></tr>
<tr><td>CMI_10</td><td>0.5</td><td>7.5</td><td>12.5</td><td>25</td><td>0.8</td><td>4.2</td></tr>
<tr><td>CMI_15</td><td>0.5</td><td>6.7</td><td>12.5</td><td>25</td><td>1.6</td><td>4.2</td></tr>
<tr><th colspan="7">MIX-DESIGN II</th></tr>
<tr><th></th><th>W/(CEM+MD)</th><th>CEM</th><th>FA</th><th>CA</th><th>MD</th><th>WATER</th></tr>
<tr><td>CMII_0</td><td>0.55</td><td>8.6</td><td>24.7</td><td>24.4</td><td>0</td><td>4.7</td></tr>
<tr><td>CMII_5</td><td>0.55</td><td>8.1</td><td>24.7</td><td>24.4</td><td>0.5</td><td>4.7</td></tr>
<tr><td>CMII_10</td><td>0.55</td><td>7.7</td><td>24.7</td><td>24.4</td><td>0.9</td><td>4.7</td></tr>
<tr><td>CMII_15</td><td>0.55</td><td>7.3</td><td>24.7</td><td>24.4</td><td>1.3</td><td>4.7</td></tr>
</table>



a) *b)* *c)* *d)*

Figure 5.5: Pie charts a) CMI_0 b) CMI_5 c) CMI_10 d) CMI_15



a) *b)* *c)* *d)*

Figure 5.6: Pie charts a) CMII_0 b) CMII_5 c) CMII_10 d) CMII_15

All the components were put in a concrete mixer for 15 minutes. When initially mixed together, Portland cement and water rapidly form a gel, formed of tangled chains of interlocking crystals. These continue to react over time, with the initially fluid gel often aiding in placement by improving workability. As the concrete sets, the chains of crystals join up, and form a rigid structure, gluing the aggregate particles in place.

After that, fresh concrete was cast into cylindrical stainless steel moulds (Φ = 150 mm, H = 300 mm) without any vibration.

The cone was filled in three phases and a bar was used to compact the concrete and remove air voids, within the cone, picking 25 times.

Three cylindrical specimens were prepared from each of the eight concrete mixtures, for a total number of 24.

The specimens poured into the moulds were held for 24 h, after that were removed from the moulds. After demolding, they were brought in a moist chamber.

5.3.3 Curing

The curing process develops physical and chemical properties. Among other qualities, mechanical strength, low moisture permeability, and chemical and volumetric stability.

During curing, more of the cement reacts with the residual water (hydration). The cement paste hardens over time, initially setting and becoming rigid though very weak, and gaining in strength in following days and weeks. In around 3 weeks, over 90% of the final strength is typically reached, though it may continue to strengthen for decades (Veretennykov et al., 2008). During this period concrete needs to be in conditions with a controlled temperature and humid atmosphere (Figures 5.7 and 5.8).

Cement requires a moist, controlled environment to gain strength and harden fully, so the test specimens were submerged concrete in water and were cured in a moist chamber with temperature at 23°C ± 2°C and relative humidity at 50 ± 2% (Marras et al., 2010). This type of curing is generally used for curing specimens for strength tests, and it’s conform with the UNI EN 12390-2.

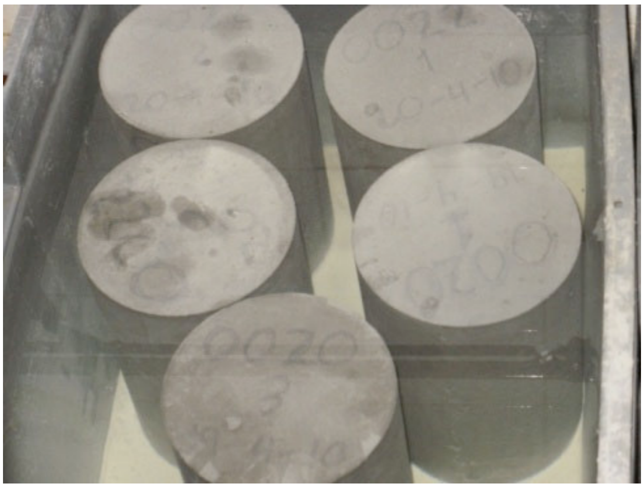


Figure 5.7: Specimens curing.

Figure 5.8: Console of regulation of environmental conditions in the moist chamber. (Martin, J. 2010).

5.3.4 Capping

Before doing the strength tests the upper ends of the cylinders were struck off with a sulfur mixture method (UNI EN 12390-3).

Before capping, we ensured that the surface of the specimen to be capped was in a dry condition, clean and all loose particles were removed. The caps would have been as thin as possible and should not have been greater than 5 mm thick, although small local deviations were permissible.

We used proprietary sulfur capping mixtures. We heated the mixture to a temperature where, whilst stirring continuously, the required consistency was reached.

The mixture was stirred continuously to ensure its homogeneity and to avoid sediment forming at the bottom of the melting pot.

The upper surfaces of the test specimens were lowered, held vertically, into a pool of molten sulfur mixture on a horizontal plate/mould, previously sprinkled with mineral oil (Figure 5.9). The mixture was allow to harden (Figure 5.10).


5.9


5.10

Figure 5.9: Specimen into a pool of molten sulfur mixture. Figure 5.10: Capped specimen.

All the capped test specimens were checked to ensure that the capping material had adhered to the ends of the specimens. If a capping layer had sounded hollow, would be removed it and then repeated the capping operation.

After the last capping operation was allowed 30 min to elapse before carrying out a compression tests on the test specimens.

5.4 Testing

5.4.1 Strength Tests (UNI EN 12390-3)

5.4.1.1 Procedure

The twenty four concrete samples were studied over a 28-day period to determine the effect of the marble dust addition. Compressive strengths were evaluated with respect to percentages of waste sludge replaced with cement.

The tests were determined using a compressive testing machine (SDE: Sistemas de Ensayo, model: CME-300/SDC, 1998) with a maximum capacity of 2,500 kN and were carried out under laboratory conditions. Strains were measured on a base of 150 mm.

All testing machine bearing surfaces were cleaned and were removed any loose grit or other extraneous material from the surfaces of the specimen that was in contact with the platens. The excess moisture was wiped from the surface of the specimen before placing in the testing machine.

The specimen was centered with respect to the lower platen to an accuracy of 1 % of the designated diameter of cylindrical specimens. The specimen was loaded in the machine and preloaded it with a constant rate of loading within the range 0.6 ± 0.2 MPa/s.

When the specimen fails, read the maximum load that the specimen withstood and record. Clean up the machine after use. The procedure above was repeated for each cylinder to determine the strength of the concrete.

5.4.1.2 Expression of results

The compressive strength is given by the equation 5.1:

$$f_c = F / A_c \qquad (5.1)$$

where

f_c is the compressive strength, in MPa (N/mm²);

F is the maximum load at failure, in N;

A_c is the cross-sectional area of the specimen on which the compressive force acts, calculated from the designated size of the specimen (see UNI EN 12390-1) or from measurements on the specimen if tested according to Annex B of the UNI EN 12390-3, in mm^2.

The compressive strength was expressed to the nearest 0.1 MPa (N/mm²).

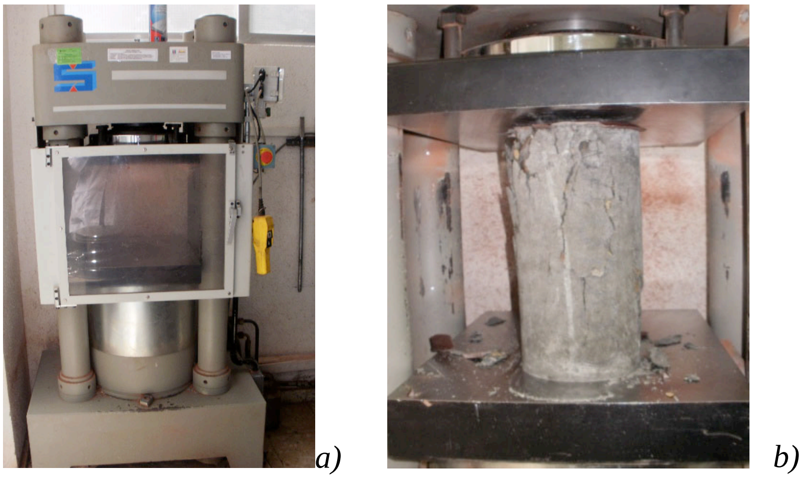


Figure 5.11: a) Compressive test machine. b) Specimen rupture.

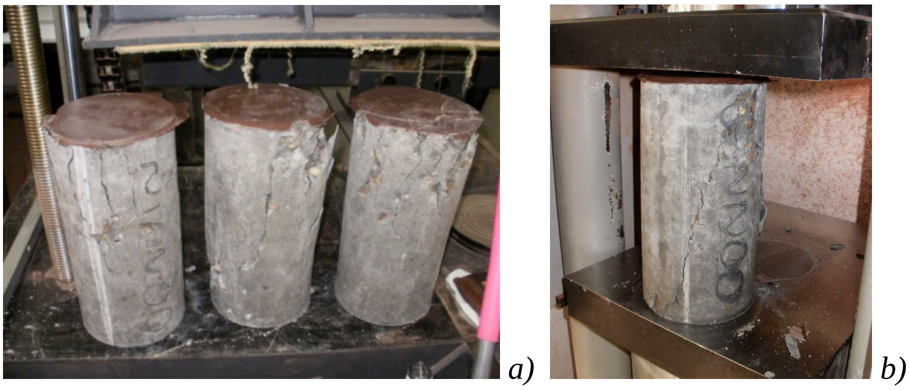


Figure 5.12: a) and b): Specimens after compressive test.

The results of the tests carried out in LOEMCO laboratory for the compressive strength at 28 days of age are listed in the Tables and Figure below (Tables 5.11 and 5.12; Figure 5.13).

Table 5.11: Compressive test data for mix-design I [MPa]

Mix-design I	**Specimen 1**	**Specimen 2**	**Specimen 3**	**Average value**
CMI_0	41.05	38.85	37.44	39.12
CMI_5	41.29	39.28	38.56	39.71
CMI_10	32.62	35.45	35.42	34.50
CMI_15	33.45	27.90	31.43	30.93

Table 5.12: Compressive test data for mix-design II [MPa]

Mix-design II	**Specimen 1**	**Specimen 2**	**Specimen 3**	**Average value**
CMII_0	28.74	27.77	27.88	28.13
CMII_5	27.46	27.61	27.18	27.41
CMII_10	23.69	24.75	23.78	24.07
CMII_15	19.07	18.98	19.16	19.07

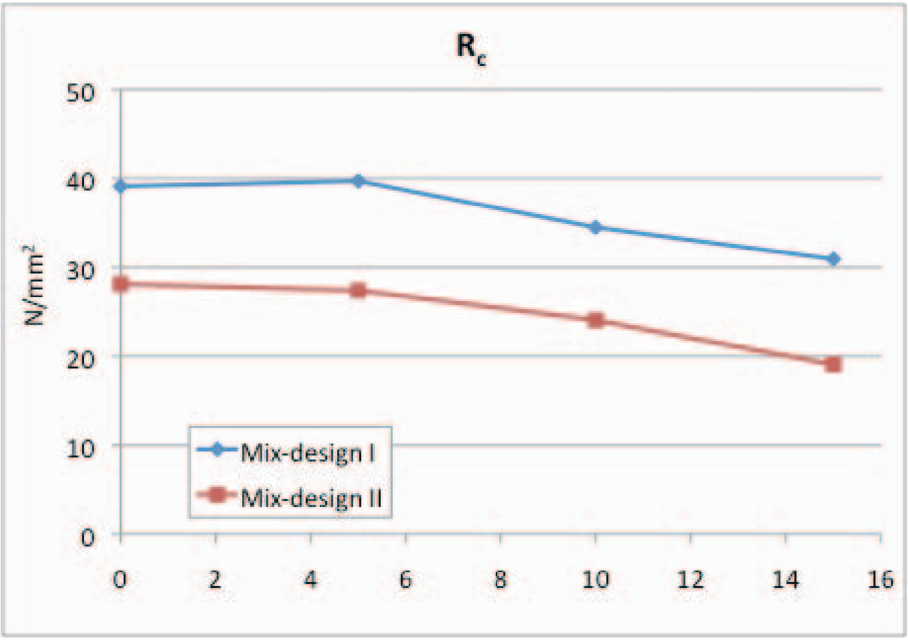


Figure 5.13: Compressive strength curves for both mix-designs.

5.4.1.3 SEM Observations

The scanning electron microscope was used to verify the reaction in the different cured specimens. It’s important noticed that when measuring mortar or other cementitious materials the question arises whether the results of the non-destructive measurements are coherent with visual parameters describing the hydration process in the material.

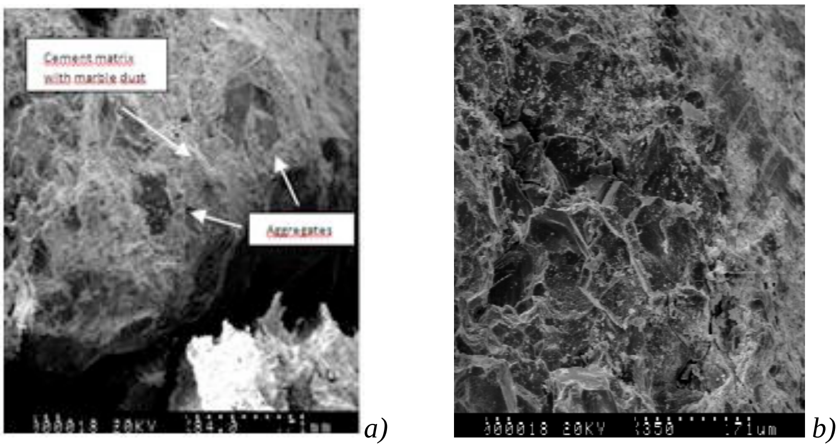


Figure 5.14: a) Microstructure of CMI_5 at 28 days (80x).

b) Microstructure of CMI_5 at 28 days (80x).

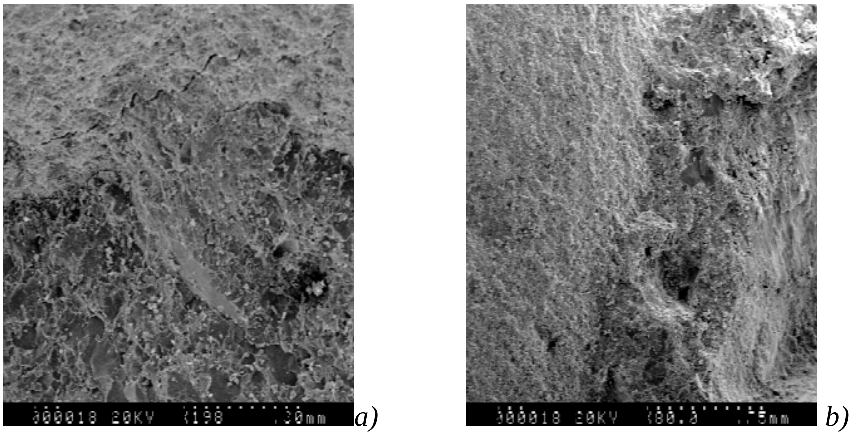


Figure 5.15: a) Microstructure of CMI_10 at 28 days (80x).

b)Microstructure of CMI_0 at 28 days (80x)

In Figure 5.14 is shown the microstructure of the concrete mixture CMI_5, after 28 days of curing and in Figure 5.15 the microstructure respectively of CMI_10 and CMI_0 past 28 days in the moist chamber.

5.5 Results And Discussions

5.5.1 Freshly mixtures property

The workability of fresh concrete was measured in terms of slump, slump flow value which is presented in Table 5.13. Slump flow for mix-designI I varying from 49 mm to 40 mm and for mix-design II varying from 50 to 42.

The analysis of the results can be drawn that the consistency of the mixture is plastic (3 to 5 cm), and that this would satisfy the conditions imposed on the mixing.

Also it can be seen that the replacement of cement by marble dust reduces the slump, but within the limits of plastic consistency.

Table 5.13: Slump Ranges for Specific Applications (after ACI, 2000)

Type of Construction	**Slump**
	[mm]
Reinforced foundation walls and footings	25 - 75
Plain footings, caissons and substructure walls	25 - 75
Beams and reinforced walls	25 - 100
Building columns	25 - 100
Pavements and slabs	25 - 75
Mass concrete	25 - 50

5.5.2 Hardened mixture properties - Compressive strength

The tests are proceeded satisfactorily. The results are compiled in Tables 5.11 and 5.12. Compressive strength were obtained as per UNI EN 12390-3.

Examples of the failure of specimen showing that the tests have proceeded adequately are given in Figure 5.16.

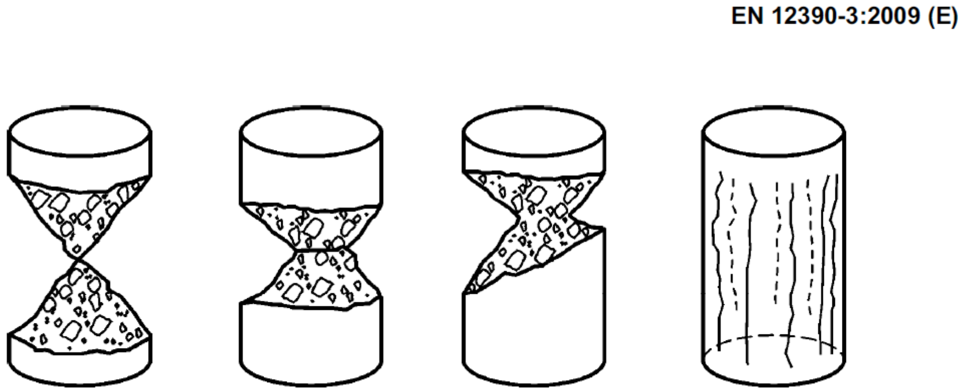


Figure 5.16: Examples of the failures of cylinder specimens.

Generally, compared to plain concrete with the same W/C ratio and cement type, concrete with high limestone filler content with suitable particle size distribution possesses improved strength characteristics (Sonerbi et al., 2000; Petterson 2001).

All the results obtained for the compressive tests are acceptable. The strength development characteristics were affected by dust percentages.

As shown in Tables 5.11 and 5.12 and in Figure 5.13 the maximum compressive value was observed for specimens containing a 5% waste sludge. In the case of 10% of replacement the compressive strength decreased and more in the case of 15%. So it was observed in Table 5.11 that there was a reduction in the compressive strength with increasing MD content.

5.5.3 SEM determinations

The well bonded interfacial zone is a characteristic of higher strength development of the concrete. Analyzing the SEM photos, it’s clearly visible the hydration of cement paste, in particular for CMI_5 (Figure 5.14). It can be observed that the marble sludge powder had a high specific surface area; this could mean that is addition should confer more cohesiveness to mortars and concrete. The reaction between aggregate and cement-paste is not totally completed in fact is discernible the dark colour in the core which is a symptom of a no-reaction zone, instead of the clear zone that has already got reaction. Nevertheless, the reaction is in progress.

In the CMI_10 the aggregate borders look corroded, and this is a sign of good reaction (Figure 5.15). Despite that pores are visible within the matrix, it creates a reduction in compressive strength. This may be due to the smaller amount of cement used.

Moreover, even if a good bond between cement - marble dust matrix and the aggregates is occurred, after 28 days of hydration, the distribution of aggregates after compaction is inhomogeneous due to the influence of manual vibration. As a result, sometimes gradients of strength may be significant.

5.6 Conclusions

The high calcium carbonate and high percentages of ultrafine dust contained in the sludge examined warrant close examination in order to obtain a better economic evaluation of this processing waste and to eliminate its environmental impact.

Technical possibilities of producing concretes containing marble dust have been studied with positive results. Thus it can partially replace cement, pursuing the aim of minimize waste generation and disposal and also of producing revenue for companies. In fact cement is the most expensive concrete component, as a result if can replace cement can obtain an economical revenue.

The use of the processing waste can improve the economic performance of the enterprises alleviating the financial burden of waste disposal.

These results are of great importance because this kind of concrete requires large amounts of fine particles. Due to its high fineness of the marble sludge it provided to be very effective in assuring very good cohesiveness of concrete, as shown in the SEM determinations (Figure 5.14, 5.15). From the above study, it is concluded that the marble powder may be used as a replacement material for part of cement.

In terms of mechanical performance 5% substitution of cement by marble dust provided maximum compressive strength, after 28 days of curing, but all the results are acceptable.

The replacement of cement with 5% of marble powder and 50% gives an excellent result in strength aspect and quality aspect. The results showed that the CMI_5 mix induced higher compressive strength, after 28 days of curing. Increasing the marble sludge powder content by more than 5% affects the compressive strength of concrete.

Then, test results show that these industrial wastes are capable of improving hardened concrete performance, in proper proportions. Generally experimental concrete has relatively high compressive strength.

For the CMII_15 sample was obtained the value of 19.07 MPa. It is a medium strength mix and is known as a C20 mix. This mix is not suitable for house foundations.

The results presented and discussed along this work enable to draw the conclusions that the compressive strength of test concrete is slightly higher than conventional concrete for the sample with the 5% replacement and that the high tonnage of raw materials consumed in the fabrication of concrete make their formulations suitable matrixes to incorporate this kind of residue replacing nonrenewable natural resources.

Therefore, the results of this study provide a strong recommendation for the use of marble sludge powder in concrete manufacturing and the final result is encouraging.

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6. BRICK MAKING

6.1 Generality

This part of research intends to discuss some technical aspects concerning the use of sludge in the ceramic raw material, in particular marble powder deriving from SIMIN company was used.

For a while, the ceramic industry, particularly the sector devoted to the fabrication of building products, has been the target for the incorporation of other industries rejects. Today, it is clear that some wastes are similar in composition to the natural raw materials used, and often contain materials that are not only compatible but also beneficial in the fabrication of particular products. Thus, upgrading industrial wastes to alternative raw materials becomes interesting, both technically and economically (Acchar et al., 2006; Bertolini and Celsi, 1990; Montero et al., 2008; Segadães et al., 2005; Saboya et al., 2006; Torres et al., 2004) and is becoming common practice.

Initially, this Chapter describes the mix-designs preparation obtained adding marble slurry in brick composition, by trial and subsequent adjustments, containing the maximum reasonable proportion; subsequently the influence of its addition on brick properties, such as shrinkage and water absorption and finally to make a comparison with control brick.

6.1.1 The brick-making process

The process of making brick generally consists of the following steps: gathering, crushing, grinding, screening, and mixing the raw materials; making the brick; and setting, drying, firing, packaging and inventorying the final product.

The manufacturing of brick begins with the gathering of surface clays and shale from the quarry. The crusher breaks up the large chunks of clay or shale and passes it to conveyors heading for the grinders that pulverize the material to a fine consistency. The pulverized material passes over a vibrating screen in which the fine material passes through to the next step and the coarse material is returned to the grinder to be reground. Once screened, the material is sent to the pug mill where it will be tempered to make a homogeneous plastic mass ready for shaping in the required brick form. Water is added to provide the proper plasticity and materials, such as manganese, are added to change the body color.

The next step is to make the material into the shape of the brick. There are three basic methods that can be used to shape the material: handmade, machine molded or extruded.

After the brick unit is formed, the units are hand or mechanically set onto kiln cars. Prior to entering the kiln, the unfired brick must be properly dried. This is an extremely important part of the manufacturing process. Moisture in the brick must be limited at this time to prevent scumming and certain mechanical defects from occurring when the brick is subjected to the intense heat of the kiln. Generally, the drying process is done by placing the unfired brick in enclosed dryers which utilize excess heat from the cooling kiln. Water in drying is removed for several reasons. First, there will be less cracking in fired bricks with less water content. Second, additional fuel is needed, beyond what is used for firing, to dry the bricks in the kiln.

For best results, drying should be done slowly. This will help with more even drying. Also, the best drying technique may change from location to location, so the brickmakers must gain experience to determine the best way to dry bricks for each production process.

The next step is burning or firing the unfired brick. It passes through the long length of the kiln. The preheating, burning and cooling is done in zones varying in temperatures up to 2,000 degrees.

After exiting the kiln, the brick is allowed to cool prior to handling. Proper sorting ("dehacking") and packaging of the brick after burning is extremely important. The finished products are lastly packaged.

6.2 Materials and Methods

As written before, the filter press sludge used for preparing the paste are coming from the SIMIN plant, they have not been subjected to any previous treatment and were analysed in Chapter 5.

Thus, part of the experimentation phase was conducted in the technological laboratory belonging to the INPREDIL S.p.A. company (Sardinia – Italy), "Geoceramic researches” operating in brick making field.

6.2.1 Brick Clays

6.2.1.1 Yellow Clay of Monastir

This name merchandise is related to the place of origin of the clay and due to its colour. Thus in the trials that clay was called YCM. It is characterized by size distribution reported in Appendix 4.A and by chemical determinations listed in Table 6.1.

Atterberg limits were studied: Lp = 21.2%; Ll = 32.4%; Ip = 11.1%.

The clay has a middle plasticity, that is confirmed by good behavior during drying, moreover, has been shown to have a drying sensitivity of 7 cm.

Table 6.1: Chemical data for yellow clay of Monastir.

COMPONENTS	**YCM [%]**
SiO_2	56.00
Al_2O_3	11.40
TiO_2	0.65
Fe_2O_3	5.63
CaO	8.63
MgO	2.13
K_2O	3.53
Na_2O	0.74
S	0.002
Fl	0.071
Cl	0.023
SiO_2	56.00

6.2.1.2 Black Clay of Ussana

Even this name merchandise comes from places of origin. Thus in the trials that clay was called BCU. It is characterized by size distribution reported in Appendix 4.B and by chemical determinations listed in Table 6.2.

Atterberg limits were studied: Lp = 19.8%; Ll = 39.1%; Ip = 19,3%.

BCU has a high plasticity that certainly does not prevent a good behavior in drying. In addition it has been shown to have a drying sensitivity of 0 cm.

Table 6.2: Chemical data for black clay of Ussana.

COMPONENTS	BCM [%]
SiO_2	63.66
Al_2O_3	15.95
TiO_2	0.92
Fe_2O_3	8.30
CaO	0.41
MgO	1.64
K_2O	4.00
Na_2O	1.00
S	nd
Fl	nd
Cl	0.48

6.2.2 Marble Dust

Cf. Chapter 4.

6.2.3 Water

A tap water available in the concrete laboratory was used, the qualities of water samples are uniform and potable.

6.3 Preparation and casting of test specimens

In this study were used the two different types of clays illustrated above and marble dust.

Taking into account previous studies concerning the incorporation of residues in red clay ceramic formulations (Menezes et al., 2005; Gupta, 2005) several batches, based on these two clays, incorporating up to 10 wt.% of marble dust were prepared (Table 6.3 and Figure 6.1). A commercial reference paste, supplied by INPREDIL S.p.A. (Italy), was used for comparison purposes.

The INPREDIL S.p.A. generally prepares its brick for walls, structures and floors, by mixing a combination of clay having the following composition:

- 60 wt. % Yellow Clay of Monastir (YCM);
- 40 wt. % Black Clay of Ussana (BCU).

Water is added at the mixture in quantity ranging from 15 - 16 % by weight as a function of moisture already by the clay. The addition of water is dictated by the need to make the paste workable, and too much amount would be cause loss of workability and a reduction of the strength of the material. Over water could be lead to the formation of cracks since the drying treatment.

Figure 6.1: Mix-design components.

BCU was kept constant in the tested formulations because it is the main clay component in ceramic INPREDIL S.p.A. paste and gives the brick structure.

The clays were previously sieved to 200 mesh sieve. As mentioned before the BCU gives the brick structure so the percentage of marble powder added was simultaneously removed from YCM. In the following table are listed the mix-designs:

Table 6.3: Mix-designs

MIX-DESIGN	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. More in details, batches were prepared as follows: the dried raw materials were weighted, mixed and moistured with 16 – 17 wt. % water.

The mix design which allowed to obtain better workability with the highest percentage of substitution of clay with marble dust was mix-design-C, and corresponds to a rate of 5 wt. %.

The paste bricks were cast inside into rectangular moulds with dimension of 12 x 8.5 x 2 mm.

Mix-design C was chosen as the paste 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.

Furthermore a marble dust sample brick was subjected to the same stage of drying and firing suffered from the test specimens, in order to analyze its behavior (Mix-design A).

Two notches were thus engraved on the mix-designs C and A 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 6.2).

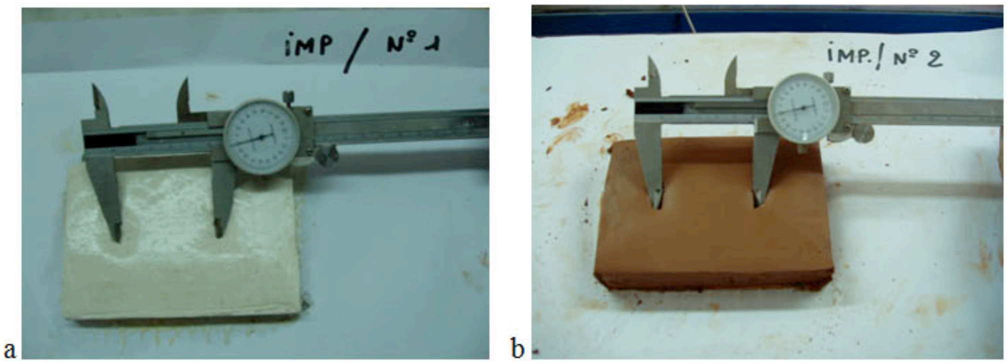

Figure 6.2: Brick sample engraving.

The homogenized mixtures were submitted at the production line.

Firstly samples were introduced for 8 hours in the dryer (Temperature: 130 °C) belonging to INPREDIL S.p.A.; secondly, the process of firing will take place in several steps. Depites, the bricks were passed in the firing section where are burned in a tunnel type furnace for 36 hours, with a curve that consistently leads the sample from room temperature at the maximum temperature 850 °C. Initially, pre-heating removed the water leftover from the drying process and this process is still physical. The second stage is firing out and out, where the clay bricks vitrified through a chemical process. The temperature remained constant at this stage for complete vitrification. Finally, for the cooling stage, the temperature has been keeping as slow and steady.

6.4 Specimen analysis

6.4.1 Shrinkage

During brickmaking a necessary consideration must be shrinkage. Bricks will shrink both when drying and firing. Thus, these samples were marked with 50 mm distance scratches to measure this important properties. At the end of the drying - process, they were analyzed for the shrinkage and weight variation.

Even after the firing step, was immediately observed shrinkage from the samples.

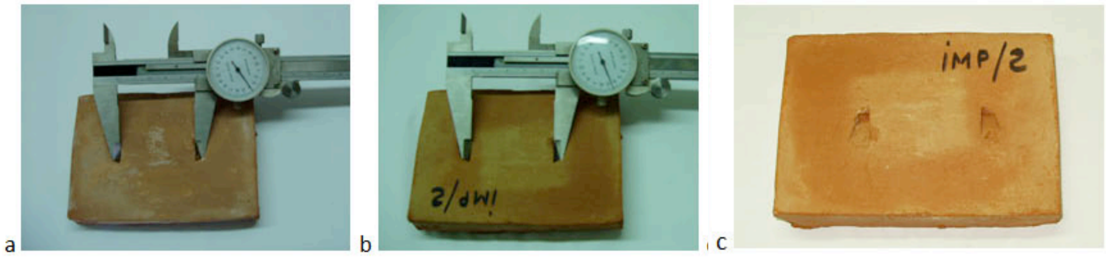

Figure 6.3: Brick sample post-drying (a), post-firing (b and c)

6.4.2 Water absorption capacity

Test on the bricks obtained was carried out to verify the properties of the specific absorption rate water absorption capacity.

As regard the calculation of specific absorption rate (a_s, imbibition, UNI EN 771-1:2004), the mix-design-C samples, after their firing, were allowed to cool in order to identify their mass G_1 and to measure the gross areas of the bearing surface F_0. The test was carried out by immersing the sample in a container with flat bottom, which holds the sample, and it was filled with water to a height maintained at a constant level of 10 mm. The sample was immersed into the tanks and was extracted after 60 ± 3 seconds and then left to drip for 45 ± 5 seconds. At this point the sample was weighed and the mass was identified called G_2.

The imbibition was determined in according to the following equation (6.1):

$$a_s = \frac{G_2 - G_1}{F_0} \quad [\mathrm{g \cdot min^{-1} \cdot dm^{-2}}] \qquad (6.1)$$

In addition, the water absorption capacity (w_a) was obtained by immersing mix-design-C samples C in water for 48 hours. The value was determined by the formula (6.2) where W_1

and W_2 are respectively the weighs before and after immersion.

$$w_a = \frac{W_2 - W_1}{W_1} \ [\%] \qquad (6.2)$$

6.5 Results and discussion

The various mix design had as objective identifying the maximum percentage of use of sawing sludge that would allow a good workability of the paste.

In Table 6.3 it can be seen how the demand for water increased, replacing YCM with marble dust, in addition, this percentage is always above the percentages required for the control INPREDIL SpA mixing (15 – 16 %).

Relatively high proportion of marble dust undermined workable, it was observed that increasing percentages of filter press sludge, the mixture was not homogeneous and workable. Applications have been excluded with substitutions above 10% would have been compromised because of the color characteristics of the product.

Specifically, the mix design A was characterized by variations in colour and low consistency, so the sludge content was proceeded gradually reduced.

6.5.1 Determinations on clays

The data of chemical composition of the raw materials are presented in Tables 6.1 and 6.2. It can be observed that in all of them, SiO_2 is the predominant oxide, followed by Al_2O_3.

YCM medium carbonate content and a moderate presence of total soluble salts, while having a significant presence of iron, calcium (bound to carbonates), and potassium.

According to the particle size point of view, prevails clay fraction (almost 60%), with a sandy fraction of 10%, approximately.

While BCU is rich in iron and aluminum, as can be seen in Table 7.2, this feature gives the clay a greater resistance to bending in both dry and cooked. Besides, BCU has a middle - low content of carbonates but a significant presence of total soluble salts, more rich in silica and lower in calcium and potassium than YCM.

6.5.2 Determinations on test specimens

The moisture was calculate for the unfired sample bricks and the average value was reported in Table 6.4.

Table 6.4: Moisture determination.

Initial Weight [kg]	**Final Weight [kg]**	**Weight Variation [kg]**	**Moisture [%]**
0.4769	0.3967	0.0802	16.8

The Table 6.5 illustrates the shrinkage for the brick samples after drying and after firing, average value was reported.

Table 6.5: Shrinkage determination.

Shrinkage Measurement		**Shrinkage [mm]**	**Shrinkage [%]**
Starting Length [mm]	50	——	——
Drying Length [mm]	47.2	2.8	5.6
Firing Length [mm]	47	0.2	0.42

As regards mix-design-C samples, after drying, the average 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 g·min^{-1}·dm^{-2} g·mindm2while water absorption percentage was 13.8 % (cf. Table 6.6). It is important noticed that a standard brick made by INPREDIL S.p.A. has the following values: a_s = 0.37 g·min^{-1}·dm^{-2} and w_a = 14 %. The presenting results are the average of 4 tested samples.

Table 6.6: Water absorption and specific absorption rate on mix-design-C samples.

Shrinkage Measurement		**Specific Absorption Rate** **[g·min^{-1}·dm^{-2}]**	**Water Absorption** **[%]**
Starting Weigth [g]	3,611	0.31	13.8
Final weigth [g]	3,914		
Bearing Surface [dm^2]	979.4		

As seen from the results, the mix-design-C sample 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.

Water absorption can be regarded as an indirect method to predict the technological properties of the final products since the measured values are closely related to the microstructure of the manufactured sample.

6.5.3 Determinations on marble sample brick

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. The moisture was calculate for the unfired marble dust sample brick and the value was reported in Table 6.7.

Table 6.7: Moisture determination.

Initial Weight [kg]	**Final Weight [kg]**	**Weight Variation [kg]**	**Moisture [%]**
0.3908	0.2853	0.1055	26.9

The Table 6.8 illustrates the shrinkage for the marble dust brick after drying and after firing, value was reported.

Table 6.8: Shrinkage determination.

Shrinkage Measurement		**Shrinkage [mm]**	**Shrinkage [%]**
Starting Length [mm]	50	——	——
Drying Length [mm]	47.9	2.1	4.20
Firing Length [mm]	47	0.9	1.88

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 (Portlandite - $Ca(OH)_2$). The mineralogical characterization and the identification of the crystalline phases were performed through an X-ray diffractometer, a RIGAKU device with Cu-Ka radiation (copper tube operated at 30 kV and 30 mA).

Mineral phases were determined by comparison with the JCPDS index (JCPDS, 1985), and was shown in Figure 6.4.

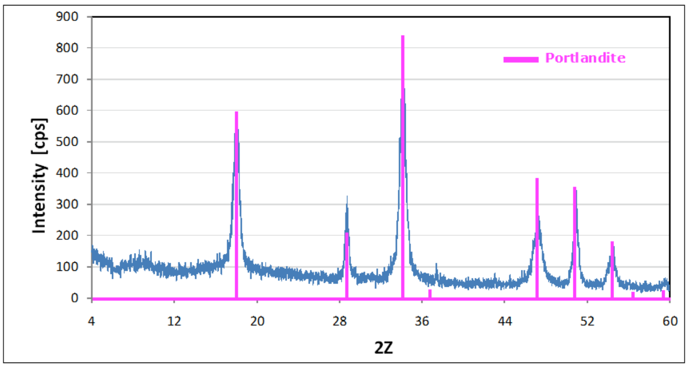

Figure 6.4: XRD spectrum after firing.

6.6 Conclusions

Results arisen from this experimentation part have demonstrated that marble wastes can get help the problem of the expansion due to humidity in ceramic materials. The application appears most interesting in this industrial for substituting of the calcium carbonate, by the marble waste mud as additive to the clay paste.

As described in the experimental part the expansion due to humidity in structural ceramic materials, is improved by the addition of calcium carbonate, in a proportion around 5 %, to the clay paste. In fact results show that paste prepared using 5 % of marble dust could be well considered, as a matter of fact the outcomes are very hopeful for mixing the marble dust in the conventional bricks making.

The experimental tests conducted on clay dried and fired sample bricks, in comparison with those of a standard brick, have showed that the use of the sludge subject of the thesis, ensures the maintenance of withdrawal both in drying and firing processes.

This application would imply a massive use of the marble wastes and would be both technically and economically feasible.

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7. GYPSUM PLASTER

7.1 Introduction

The general term of gypsum (derived from the greek γύπσος) indicates either two substances are known and used for millennia, since the time of the Egyptians: both a mineral and industrial products derived from it.

Gypsum is a very soft mineral composed of calcium sulfate dihydrate, with the chemical formula:

$CaSO_4 \cdot 2\ H_2O$.

Gypsum is a particularly useful processed material. Its main application is as a building material, its main derived product is *stucco or plaster* for plastering walls and making decorative features in buildings. However gypsum also has a diversity of other uses including making writing chalk, soil conditioning for agriculture, making moulds for pottery, as an additive in the manufacture of Ordinary Portland Cement, in surgical splints, in increasing the hardness of water, as an additive in certain foods such as *tofu* and in some types of medicines and pharmaceuticals. Its own construction use can also include external applications, such as in making walling blocks, where the climate is generally dry and not prone to the dampness, because the humidity does damage to common types of gypsum.

7.2 Plaster - Gypsum plaster

The term *plaster* can refer to gypsum plaster. Plaster is a building material similar to mortar or cement. Like those materials, plaster starts as a dry powder that is mixed with water to form a paste which liberates heat and then hardens. Unlike mortar and cement, plaster remains quite soft after setting, and can be easily manipulated with metal tools or even sandpaper. These characteristics make plaster suitable for a finishing, rather than a load-bearing material.

7.2.1 Plaster production process

Gypsum rock is converted into gypsum plaster by driving off some of the chemically combined water. Heating gypsum for one hour results in a hemihydrates, with three quarters of the water removed. Prolonged heating over several hours results in the formation of anhydrite with practically none of the chemically combined water left. Anhydrite sets more slowly and is a slightly stronger plaster than hemihydrate, but with the drawback of added production cost. In practice, a simple production system would most likely give a mixture of the hemihydrate and anhydrite phases. Gypsum plaster sets by chemically combining with water to form solid calcium sulphate dihydrate.

A special type of plaster, called alpha hemi-hydrate, can be produced by reacting the raw material under high pressure steam in strictly controlled conditions. This plaster sets harder and is used in dental work and as a modelling plaster, but is impossible to produce without expensive production equipment.

In details, the plaster is obtained by heating natural gypsum to 128 °C, thus making its essential constituent, the calcium sulfate dihydrate, loses half a molecule of crystallization water and thus occurs the transformation into gypsum hemihydrate, whose chemical formula is $CaSO_4 \cdot \frac{1}{2}\ H_2O$ and it is also known as *Plaster of Paris*, because the gypsum from the quarries of the Montmartre district of Paris has long furnished burnt gypsum used for various purposes. Much of the commercial plaster produced industrially today is plaster of Paris. It has a specific gravity of 24.52 – 26.49 N/dm^3 and contains 5 – 7 % water. Pulverized and mixed with water, easily takes the water lost and sets forming a compact crystal aggregates.

Thus, Plaster of Paris is calcium sulphate hemihydrate, it is created by heating gypsum to about 150 °C, as shown in the following chemical reactions (Turco, 1996):

$$CaSO_4 \cdot 2\ H_2O \quad \rightarrow \quad CaSO_4 \cdot \tfrac{1}{2}\ H_2O + 1\ \tfrac{1}{2}\ H_2O \text{ (released as steam)}$$

The resultant plaster will set hard in a few minutes after the addition of water, some of which is re-combined chemically so that in effect the set plaster is identical in composition to the original gypsum. When the dry plaster powder is mixed with water, it re-forms into gypsum.

With further heating to 163 °C (in practice be reached or exceeded 200 °C), calcium sulphate hemihydrate obtained first at 128 °C loses all water of crystallization and becomes calcium sulfate anhydrous, soluble, by chemical formula $CaSO_4$. This leads to the soluble anhydrite or anhydrite α, with a specific weight of 23.94 - 24.03 N/dm^3 and a pinch slower, is also known as gypsum or plaster factory building or common plaster (*plaster of Paris* in English; *yeso de costrucción* in Spanish). The behavior of the common plaster between 128 °C and 163 °C can be schematized in the following chemical reactions (Turco, 1996):

$$CaSO_4 \bullet \tfrac{1}{2} H_2O \quad \rightarrow \quad CaSO_4 + \tfrac{1}{2} H_2O \text{ (released as steam)}$$

Both processes are reversible.

7.2.2 Production of gypsum plaster

In order to achieve the desired results the mined gypsum has to be reduced in size to a fine powder by various crushing and grinding stages and, if necessary, free moisture is removed during one of these stages (Smith, R., 1986).

The resultant ground gypsum is fed to a large steel receptacle known as a kettle, where it is heated by a coal, oil or gas furnace under controlled conditions for up to two hours. This operation is known as calcination. The method used for calcining determines the type of gypsum produced. The resultant hemihydrate plaster is discharged rapidly from the kettles and passed to a series of storage silos for further use in plasterboard manufacture. In certain cases, the kettles may be operated continuously by arranging to feed ground gypsum in at one point and discharge the finished plaster at another.

The main advantage of gypsum plaster over some other binders is that temperatures of only 120 to 160°C are required during production, so high-temperature kilns are not needed.

The precise nature of gypsum plaster depends on a considerable number of factors connected with the composition of the gypsum rock, the temperature and pressure conditions, the length of calcining time, etc.

For example, if calcination occurs by heating the calcium sulfate dihydrate in an open kettle at 110 °C to 120 °C, the beta form of the hemihydrate is produced. This type has particles that are porous and irregular in shape and is found in impression plaster and, to a certain extent, model plaster. If

calcination occurs by heating the dihydrate in an autoclave at 130 °C, the alpha form of the hemihydrate is produced. This type is dense, regular, and needle-like and is found in model plaster

and regular stone. Finally, if calcination occurs by boiling the dihydrate in a 30% calcium chloride solution, the alpha form of the hemihydrate is again produced. Its crystal shape, however, is stubby in addition to being regular and dense. This particle type is found in the high-strength stones.

Setting Reaction of Gypsum

$$CaSO_4 \bullet \frac{1}{2} H_2O + 1\frac{1}{2} H_2O \rightarrow CaSO_4 \bullet 2H_2O + 3{,}900 \text{ cal/gm mole}$$

The reaction is an exothermic one.

As indicated in Table 7.1, it’s possible to classify different type of plasters according to the setting time (Lewry and Williamson, 1994; Singh and Garg, 1997).

Table. 7.1: Setting time and volume change for plaster.

Type	**Start of setting in**	**Setting time**	**Volume change**
A - fast setting	2 min	15 min	+ 1 %
B - regular setting	6 min	30 min	+ 1 %
C - slow setting	20 min	90 min	+ 2 %

7.3 Experimental Phase

In the past few decades, gypsum-based renders and plasters have become the material of choice for indoor finishing in many countries (Arikan and Sobolev, 2002). Excellent performance, attractive appearance, easy application, and its healthful contribution to living conditions have made gypsum a most popular finishing material for centuries (Arpe, 1984; Duggal, 1998; Ragsdale and Raynham, 1972).

The experimental phase was carried out, during the period of research abroad, at the Higher Technical School of Mining Engineering, Technical University of Madrid, and, in this specific case, conducted at the Department of Gypsum in LOEMCO laboratory (Madrid – Spain).

The feasibility of adding marble dust in plaster was studied by mixing the components replacing varying proportions of gypsum with marble dust and carrying out the following tests to evaluate the mechanical behavior:: consistency (water / plaster - flow table test), flexural strength, compressive strength and determination adhesion to the substrate.

7.3.1 Materials and methods

The research had focused on the possibility of adding calcium carbonate to the gypsum for making plasters, in particular projection gypsum plaster that is a gypsum plaster formulated for mechanical application, mixed with water to the required consistency and applied by projection machine to the background.

For this experimental part were prepared different mixtures obtained by replacing varying proportions of gypsum with marble dust and were conducted the following tests, according to the national standards indicated in the UNI EN 13279-2: 2004 – “Gypsum binders and gypsum plasters”, in order to evaluate the mechanical behavior of the compounds created:

1. determination of the water/plaster ratio by the flow table method;
2. determination of flexural strength;

3. determination of compressive strength;
4. determination of adhesion.

Two different types of materials were used in this research: gypsum and marble dust as aggregate.

7.3.1.1 Gypsum

Type PROYAL MAX, PLACO Company - SONEJA plant (placo.es) was used in the laboratory program. with the technical characteristics tabulated in Table 7.2.

Table 7.2: Technical characteristics of Gypsum – Proyal Max.

No.	Property	Value
1	Purity index	70 [%]
2	Grain size	0 – 1.5 [mm]
3	Water/gypsum ratio	0.5 – 0.6
4	Surface hardness	≥ 65 (shore C unit)
5	Efficiency	< 9.5 [kg/cm]
6	pH	> 6
7	Thermal conductance coefficient	0.26 [W/mK]
8	Tensile strength	≥ 1 [N/mm^2]
9	Compressive strength	> 2 [N/mm^2]
10	Adhesion	> 0.1 [N/mm^2]
11	Type of background	Traditional[1]

7.3.1.2 Aggregates

The aggregates, used for gypsum binders and gypsum plasters, are defined as natural, synthetic or recycled materials suitable for use in buildings, e.g. lightweight aggregates such as perlite or vermiculite or aggregates such as siliceous sand or calcareous crushed stone sand (UNI EN 13279-1: 2008). The aggregate used in this study was the marble slurry recovered at the exit of the filter-press section in the marble processing plants. This

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[1] Bricks, concrete and blocks

material was analyzed in the Chapter 5.

7.3.1.3 Water

A tap water available in the concrete laboratory was used in manufacturing the concrete, the public water was supplied by the aqueduct of Madrid (Isabel II).The qualities of water samples are uniform and potable.

7.3.1.4 Marble Dust

Cf. Chapter 4.

7.3.2 Determination of the water/plaster ratio with the flow table method

To set out this experimental phase, the first step had been to identify water/plaster ratio and we made this with the flow table method and for all the mix-designs created.

This method is used for premixed gypsum plasters. Generally, the water/plaster ratio is determined by the trial and error method until a pat of a specified diameter is formed, when a truncated cone, filled with the slurry, is removed and jolted in the manner described below. The water/plaster ratio for premixed gypsum plaster is defined by a given consistency. The required consistency is achieved, when the empirically determined diameter of the pat of plaster is (165 ± 5) mm.

Therefore we proceeded with this procedure for all the created mix-designs, that are listed in Table 7.2.

First of all, 500 g of the gypsum plaster was weighed to 1 g. The quantity of water determined by a water/plaster ratio of 0.6 was weighed into the dry mixing bowl.

Then, the procedure was to fold the gypsum plaster into the water and premixing with the spatula and the paddle by hand for about 1 min. The plaster was then mixed with the mixer and the paddle for 1 min at low speed (140 ± 5) min - 1 rotation and (62 ± 5) min - 1 planetary motion.

The slump cone was placed at the centre of the plate of the flow table and it was hold firmly in position with one hand (Figure 7.1). The excess of plaster was poured into the cone with a spatula.

Figure 7.1: Flow table method.

After 10 s to 15 s the slump cone was vertically withdrawn. Fifteen vertical blows was then applied to the flow table at a constant speed of 1 revolution per second.

The diameter of the resulting pat was measured to 1 mm, by mean of a caliper gauge, in two directions at right angles to each other verifying that the mean diameter was 165 ± 5 mm. When the slump differed from that specified for the product, the test was repeated from the beginning using larger or smaller quantities of water.

The water/plaster ratio R is given by formula 7.1.

$$R = m_2 / m_1 \tag{7.1}$$

where:

m_2 is the mass of mixing water, in g;

m_1 is the mass of gypsum plaster, in g.

And the final results are reported in the table below.

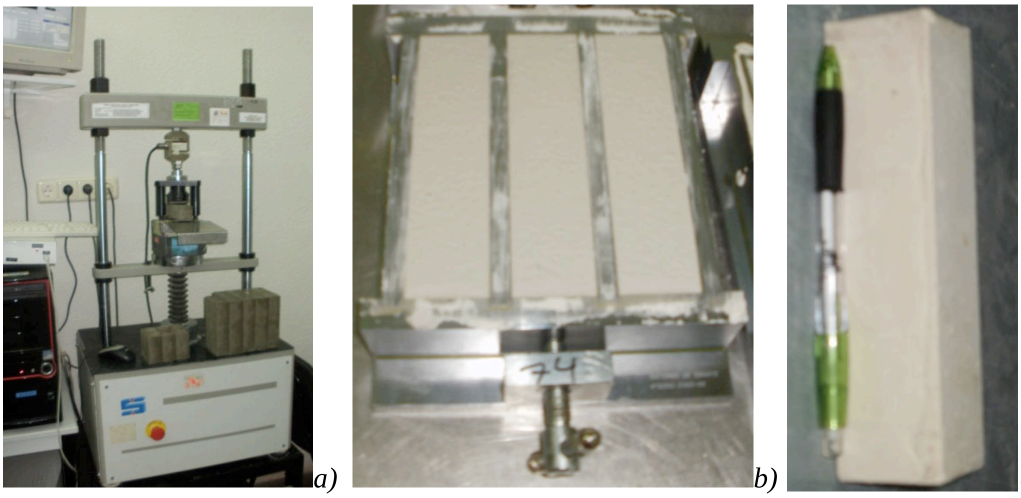
Table 7.2: Mix Designs for the experimentation on plasters and relates water/plaster ratio.

Mix Design	Gypsum wt. %	Marble dust wt. %	Water/Plaster ratio
1	100	0	0.60
2	95	5	0.60
3	90	10	0.57
4	85	15	0.55

7.3.3 Determination of flexural strength

The plasters under test were mixed using the water/plaster ratio determined in the previous paragraph and mixing also the different percentages of marble powder 0 – 5 – 10 – 15 %. Immediately after being prepared, each plaster paste was transferred using a spatula to press into the sides and corners of the mould which had previously been lightly greased. To eliminate any air-bubble the mould was raised 10 mm by its end and allowed to fall. This was repeated 5 times at each end. The moulds were filled not later than 10 minutes after the start of mixing, and the surface may not be smoothed. After setting was completed the surplus paste was scraped off with a sawing motion of the steel rule. Three prisms for each mix-design were prepared in this way and six for the control one (Figure 7.2).

When an adequate degree of strength had been reached, the prisms, identified with marks, were removed from moulds. The prisms stored 7 days in the standard atmosphere: temperature (23 ± 2) °C and relative humidity of the air (50 ± 5) %. Then, they were dried to constant mass at (40 ± 2) °C. After drying, the samples were cooled to room temperature.



a) b) c)

Figure 7.2: a) Flexural testing machine (Sistema de Ensayos); b) Molding gypsum samples; c) Test-samples for flexural strength.

7.3.3.1 Procedure

The force required to break a plaster prism 160 mm x 40 mm x 40 mm centers was determined.

The test specimens were placed on the supporting rollers of the bending device and the loading roller was applied using the test machine after the start of loading, recording the maximum load in Newton supported by the test specimens.

7.3.3.2 Expression of results

The flexural strength P_F is given by formula 7.2:

$$P_F = 0{,}00234 \times P \qquad (7.2)$$

where:

P_F is the flexural strength, in N/mm^2;

P is the average breaking load in N of at least three obtained values.

At the end, the average values obtained for the rupture in flexural strength tests are shown in the Tables 7.3, 7.4and in Figure 7.3.

Table 7.3: Figures obtained for rupture in flexural strength tests.

BREAKING LOAD, P [kN]				
Mix Design	**1**	**2**	**3**	**Mean Value**
MP0 - 1	0.63	0.64	0.65	0.56
MP0 - 2	0.54	0.45	0.47	
MP5	0.65	0.55	0.63	0.61
MP10	0.60	0.68	0.65	0.64
MP15	0.77	0.70	0.69	0.72

Table 7.4: Figures obtained for rupture in flexural strength tests.

Mix Design	Test specimen 1 P_F [N/mm^2]	Test specimen 2 P_F [N/mm^2]	Test specimen 3 P_F [N/mm^2]	Mean Value P_F [N/mm^2]
MP0 - 1	1.47	1.50	1.52	1.32
MP0 - 2	1.26	1.05	1.10	
MP5	1.52	1.29	1.47	1.43
MP10	1.40	1.59	1.52	1.51
MP15	1.80	1.64	1.61	1.68

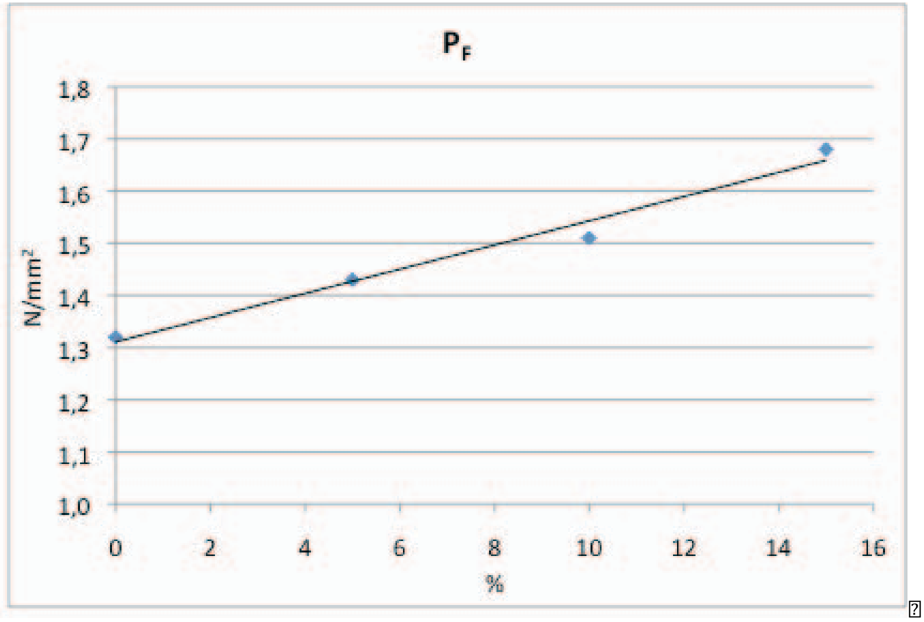


Figure 7.3: Flexural strength march.

7.3.4 Determination of compressive strength

Compressive strength was determined by applying a load to the broken parts of the test specimens used for the determination of flexural strength. The test specimens were compressed until it fails.

The test pieces were placed between the steel platens so that the sides of the prism which were in contact with the sides of the moulds were in contact with the platens over a section of 40 mm x 40 mm.

The upper platen is allowed to tilt so that perfect contact was made between the test piece and the platen. The axis of rotation of the upper platen passes through the centre of the surfaces which are being compressed. The test specimens were loaded until ruptures of the test specimens occurred.

7.3.4.1 Expression of results

The mean values of the test values were calculated and expressed in N/mm² (Table 7.5 and Table 7.6). The compressive strength R_c load is calculated by formula 7.3.

$$R_c = F_c / 1600 \tag{7.3}$$

where

R_c is the compressive strength, in N/mm^2;

F_c is the maximum load at fracture, in N;

1600 (40 mm x 40 mm) is the area of the platens in mm^2.

Table 7.5: Figures obtained for rupture in compressive strength tests.

MAXIMUM LOAD AT FRACTURE, P [kN]							
Mix Design	**1-1**	**1-2**	**2-1**	**2-2**	**3-1**	**3-2**	**Mean Value**
MP0 - 1	6.65	6.70	6.84	6.89	7.20	6.99	6.50
MP0 - 2	6.14	6.02	6.14	6.07	6.21	6.11	
MP5	6.49	6.15	6.41	6.65	6.99	6.60	6.55
MP10	7.28	7.89	7.86	7.70	7.39	7.74	7.64
MP15	7.73	7.02	7.61	8.06	6.74	6.85	7.34

Table 7.6: Figures obtained for rupture in compressive strength tests.

Mix Design	**Test specimen 1 R_c [N/mm^2]**		**Test specimen 2 R_c [N/mm^2]**		**Test specimen 3 R_c [N/mm^2]**		**Mean Value R_c [N/mm^2]**
	1-1	**1-2**	**2-1**	**2-2**	**3-1**	**3-2**	
MP0 - 1	4.16	4.19	4.28	4.31	4.50	4.37	4.06
MP0 - 2	3.84	3.76	3.84	3.79	3.88	3.82	
MP5	4.06	3.84	4.01	4.16	4.37	4.13	4.09
MP10	4.55	4.93	4.91	4.81	4.62	4.84	4.78
MP15	4.83	4.39	4.76	5.04	4.21	4.28	4.58

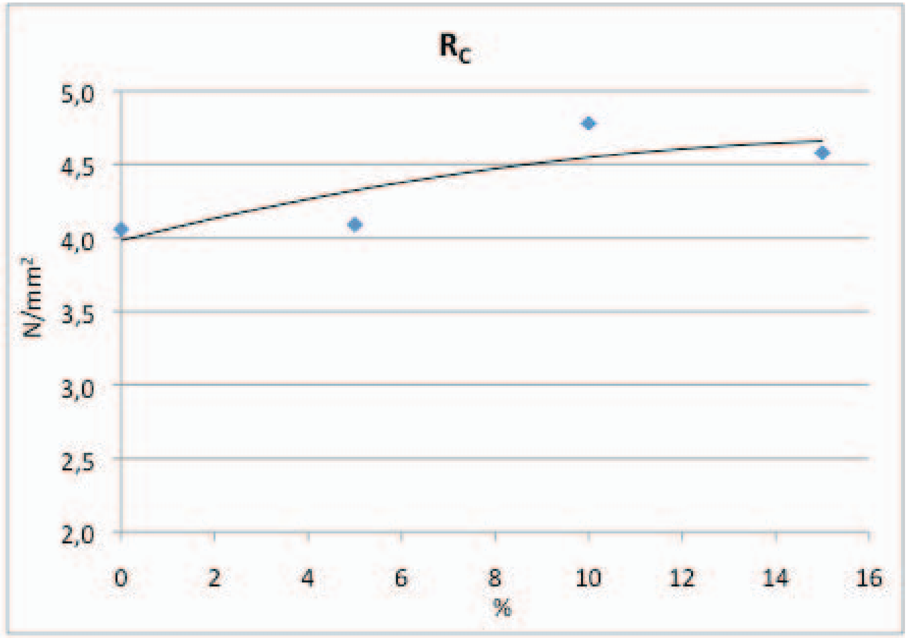


Figure 7.4: Compressive strength march.

7.3.5 Determination of adhesion

The adhesion of a plaster to a specific background is measured as the maximum load supported when a metal disc fixed to the plaster is pulled perpendicular to the surface (Figure 7.7) Bricks of size 30 x 14 x 4 [cm] were used as background surfaces.

7.3.5.1 Procedure

Background surfaces were prepared (Figure 7.5) in accordance with good practice or the appropriate code of application (UNI EN 13279-2: 2004).

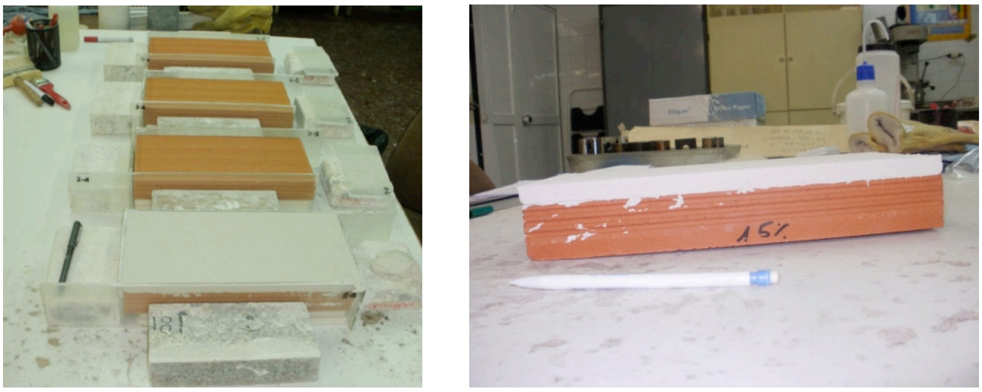


Figure 7.5: Test-samples preparation.

The plasters were mixed, using the water/plaster ratio determined in paragraph 7.3.2, with the different percentages of marble powder 0 – 5 – 10 – 15 %, and applied to the substrate. When the plaster had set the specimens was stored for seven days in the test-atmosphere: temperature (23 ± 2) °C and relative humidity of the air (50 ± 5) %. Using the circular core cutter (Figure 7.6) test areas were isolated from the surrounding plaster. The cut was made to a depth of approximately 5 mm into the background and with 50 mm ± 0,5 mm in diameter. The pull-heads were glued to the isolated area of plaster with the adhesive (*Loctite* brand., No.454), taking care to position the pull-heads centrally over the area and making sure that the adhesive does not bridge the gap between the isolated area and its surrounds (Figure 7.7). The tensile load was applied perpendicular to the test area using the testing machine. The load was applied at an uniform rate within the range 0.003 N/mm^2 to 0.1 N/mm^2 per second, at the test area of 1.963 mm^2 (ø 50 mm).

Traction device permitting a tensile force to be applied to the steel plates without subjecting the assembly to a flexural stress.

Figure 7.6: Circular core cutter.

Figure 7.7: Pull-heads for the adhesive test.

7.3.5.2 Expression of results

The individual adhesive strength was calculated by formula 7.4:

$$R_u = F_u / A \qquad (7.4)$$

where

R_u is the adhesive strength in N/mm^2;

F_u is the failure load in N;

A is the test area of the cylindrical specimen, in mm^2.

The adhesive strength was calculated as the mean value from the individual values of the specimen to the nearest 0,01 N/mm^2.

The final results are reported in the following tables.

Table 7.8: Figures obtained for adhesion tests.

Mix Design	**Test specimen 1** R_u **[N/mm^2]**	**Test specimen 2** R_u **[N/mm^2]**	**Test specimen 3** R_u **[N/mm^2]**
MP0	0.19	0.17	0.29
	Plaster	Interface	Interface
MP5	0.19	0.23	0.15
	Interface	Interface	Plaster
MP10	0.19	0.20	0.23
	Interface	Interface	Plaster
MP15	0.17	0.18	0.16
	Interface	Interface	Interface

7.4 Results and Discussion

7.4.1 Flexural strength

It can be seen that the marble dust has direct relation with the flexural strength of gypsum plaster (Table 7.4 and Figure 7.3). In fact, the use of marble powder resulted in increase in flexural strength, the average value rises from 1.32 [N/mm^2], control specimens MP0, to 1.68 [N/mm^2], MP15.

7.4.2 Compressive strength

The effect of marble dust on the compressive strength of set and hardened gypsum plaster at different percentage of substitution is shown in Table 7.6 and Figure 7.4.

Data show that at 10 % of marble dust addition, maximum attainment of strength generally was achieved which clearly manifests that in terms of compressive strength the marble powder can improve the strength in the plasters.

7.4.3 Adhesive test

In the tests carried out for adhesive strength was impossible to calculate the average values for the different figures obtained, because of the ruptures that occurred.

In fact, in some cases rupture may not occur in the correct way at the interface between mortar and substrate. For example, it can occur in the plaster itself or in the background or in the adhesive resin at the pull-head. In these cases the adhesive strength will be higher or lower than the measured value. These values shall therefore be neglected when calculating the mean value. If fracture occurs at the interface between plaster and background material, test value equals the adhesive strength, on the other hand, if it occurs in the plaster itself or in the background material, the adhesive strength is greater than the test value.

The fracture pattern shall however in each case be reported according to Figure 7.8 a), b) c) and d).

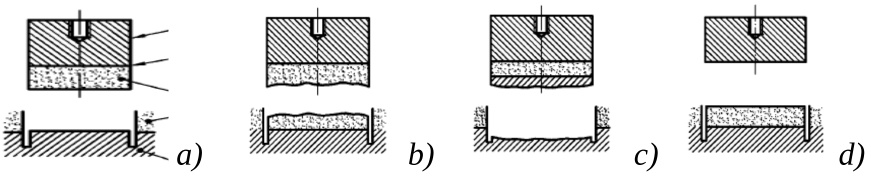


Figure 7.8: Examples of the failures (UNI EN 13279-2). a) Adhesion fracture (at the interface between plaster and background). b) Cohesion fracture (in the plaster itself). c) Cohesion fracture (in the background material). d) Fracture in the adhesive layer.

When the fracture occurs at the interface between plaster and background (Figure 7.8 a) the test value equals the adhesive strength, as in the test MP15. Only for this one, was possible to calculate the average value that results 0.17 [N/mm^2], that is an acceptable datum. For the other specimens (tests MPO specimen 2 and 3, MP5 specimen 1 and 2, MP10 specimen 1 and 2 and MP15 specimen 1, 2 and 3) were present a fracture in the plaster itself, that corresponds to an adhesive strength greater than the test value.

7.5 Conclusions

As explained before and according to the test results, the marble powder significantly increases both flexural and compressive strength.

A compressive strength loss was observed in the case of the application of the 15 % of marble dust, but the value remains considerably higher than the basic sample.

It was found that the adhesive tests may not be sufficient for the determination of adhesive strength, because of the false ruptures, as analysed in Paragraph 7.4.3.

The causes related to problems with materials are linked with the set of mechanical, physical and chemical characteristics. Consequently, improving properties is the only way to ensure their good execution and proper functioning when applied in the building.

In conclusion, the results have demonstrated that marble dust, added to gypsum plaster powder before gauging, modifies some physical properties of the binder after hardening, e.g. compressive and flexural strengths.

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UNI EN 13279-1: 2008 Gypsum binders and gypsum plasters - Part 1: Definitions and requirements.

UNI EN 13279-2: 2004 Gypsum binders and gypsum plasters - Part 2: Test methods.

Links

www.placo.es

8. EXPERIMENTAL CELLULAR BLOCKS

8.1 Generality

Autoclaved cellular concrete, also known as autoclaved aerated concrete is a type of lightweight concrete, characterized by a density lower than usual. In fact this type of concrete has a density between 400 and 2,000 kg/m^3 instead of about 2,300 - 2,600 kg/m^3 for normal concrete.

Unlike most other concrete applications, autoclaved cellular concrete is produced using no aggregate larger than sand. Quartz sand, lime, and/or cement and water are used as a binding agent. In industrial processes for reducing the concrete density, aluminium powder is used, at a rate of 0.05% – 0.08% by volume (depending on the pre-specified density). Aluminium powder reacts with calcium hydroxide and water to form hydrogen. The hydrogen gas foams and doubles the volume of the raw mix creating gas bubbles. At the end of the foaming process, the hydrogen escapes into the atmosphere and is replaced by air. Depending on its density, up to 80% of the volume of an autoclaved cellular concrete block is air.

In addition, aggregates commonly used are finely ground resulting in a fine powder, usually the same order of fineness of cement (Pacenti, V., 1966), so the use of sludge in question seemed to be appropriate.

8.2 Materials and Methods

The goal of this part of the experimentation was to demonstrate the feasibility of using sawing sludge as a byproduct in packaging lightweight blocks, which we have called "experimental cellular blocks". The research was conducted with the limit of the absence of an autoclave, so we carried out a comparison with a sample of Gasbeton®, a commercial lightweight concrete, but taking into account that the comparison has some gaps.

Since the research is ongoing, exclusive of an entrepreneur operating in the Orosei Marble District, it was not possible to publish the mix design created, so the paste comprises the components listed below, in undisclosed proportions.

The experimental cellular blocks were made mixing the following components:

- Mable sludge;
- Portland Cement;

- Aluminium foam;
- Water.

Mable sludge was analysed in Chapter 4. Sawing mud was used in proportions varying from 90% to 70% by weight in the mix design.

Cement used was a Portland cement type I 52.5 R, COLACEM (conforming to UNI EN 197-1), characterized by a mass percentage of clinker varies from 95 to 100%.

Aluminium foam was a commercial type.

A tap of w*ater* available in the Orosei plant was used. The qualities of water samples are uniform and potable.

8.3 Making “experimental cellular blocks”

All the components were put in a concrete mixer for 10 minutes. When initially mixed together, Portland cement and water rapidly form a gel, formed of tangled chains of interlocking crystals. These continue to react over time, with the initially fluid gel often aiding in placement by improving workability. As the concrete sets, the chains of crystals join up, and form a rigid structure, gluing the aggregate particles in place.

After that, fresh concrete was cast into wooden moulds having dimensions of 40 x 25 x 10 [cm] without any vibration. Each mould was filled in two phases.

The specimens poured into the moulds were held for 24 h, after that were removed from the moulds.

Past 47 minutes there was the aging of the experimental cell block and 9 hours later the mass has reached an enough hardness for demolding (Fig. 8.1).

Figure 8.1: Experimental cellular blocks after demolding.

8.4 Experimental analysis

On the blocks were carried out chemical, physical and mineralogical analyses in order to put them in comparison with those of products currently on the market (gasbeton.it).

8.4.1 Chemical characterization

The chemical analysis was reported in Table 8.1, and was made by “Laboratorio Chimico del Nuorese”.

Table 8.1: Chemical data.

Elements	**[mg/kg]**
Ar	0.09
Al	26.5
B	11.0
Ba	1.1
Ca	3,170
Cd	0.08
Co	0.32
Cr	0.32
Cu	1.2
Fe	130.5
K	36.6
Mg	1,188
Mn	13.6

Na	77.2
Ni	1.4
Pb	0.07
V	1.0
Zn	5.8
pH	9.03

8.4.2 Physical characterization

8.4.2.1 Density

Density is defined as the weight (mass) per unit of volume used as a measure of the compactness of a substance (glossary.oilfield.slb.com). It is commonly expressed as kilograms per cubic meter (kg/m^3) or pounds per cubic foot (lb/ft^3). Mean density is computed by the formula $D = m \div V$ where 'm' is the mass of a substance and 'V' is its volume. Relative density (also called specific gravity) is the ratio of the density of a substance at 20°C to the density of water at 4°C.

Mathematically, density is defined as mass divided by volume (Formula 8.1):

$$\rho = m/V \qquad (8.1)$$

with:

m = sample mass [kg];

V = sample volume [m^3].

The bulk density is the weight of an unit volume of a loose material (such as a powder or soil) to the same volume of water (glossary.oilfield.slb.com). It’s expressed in kilograms per cubic meter (kg/m^3) or pounds per cubic foot (lb/ft^3).

The bulk density for the two representative samples were analyzed, one for each material under study. First of all the samples weights were recorded. One couple of samples was saturated and the other one was waterproofed by silicone primer (SIL707 - *Baldine Vernice*); thereafter, the samples were submerged in a graduate cylinder filled with water, without spilling, from which could be traced to the volume of samples from the volume of water spilled, and consequently was derived the volume of the samples.

The results reported in Table 8.2 are referred to both the methods, respectively saturation method and waterproofing one.

Table. 8.2: Gasbeton® and "experimental cellular blocks" bulk densities.

SAMPLE	Mass [g]	Volume [cm^3]	Bulk density [g/cm^3]	Mean bulk density [g/cm^3]
Gasbeton®	11.9	22.84	0.52	0.515
	16.6	32.25	0.51	
Experimental Cellular Block	25.7	36.81	0.70	0.71
	22.2	39.72	0.72	

Was also calculated both the absolute gravity of the experimental cellular block and the filter-press mud, thanks to a pycnometer, AccuPyc 1330 V2.01, manufactured by Micrometrics Instruments. Data shown in Table 8.3 underlining that the testing has been conducted at a temperature of 19 °C with a number of cycles equal to twenty in a cell and in an exposure chamber having respectively volume of 11.93 cm^3 and 8.22 cm^3.

Table 8.3: Gasbeton® and "experimental cellular blocks" absolute gravity.

SAMPLE	Volume [cm^3]	Absolute gravity [g/cm^3]	Mean Volume [cm^3]	Mean absolute gravity [g/cm^3]
Gasbeton®	2.0495	2.4419	2.05	2.44
	2.0481	2.4436		
Experimental Cellular Block	2.0498	2.4316	2.05	2.43
	2.0523	2.4286		
	2.0521	2.4289		
Marble sludge	3.3894	2.6604	3.39	2.66
	3.3884	2.6612		

8.4.2.2 Porosity

Porosity is the percentage of pore volume or void space. Effective porosity is the interconnected pore volume ck that contributes to fluid flow in a reservoir. It excludes isolated pores. Total porosity is the total void space in the rock whether or not it contributes to fluid flow. Thus, effective porosity is typically less than total porosity (glossary.oilfield.slb.com).

The porosity of a material is a scalar quantity and is generally defined as the ratio between the volume of voids V_p (pores) and the total volume of material V_m (Formula 8.2):

$$\Phi = V_p / V_m \qquad (8.2)$$

It is inversely related to bulk density. Bulk insulation, mechanical strength, durability and permeability of materials also depend on porosity.

This characteristic was studied for Gasbeton® and experimental cellular block in order to compare this currently marketed product with test specimen, also to determine some parameters to improve in making experimental cellular block, and thus make it suitable. The results obtained are reported in Table 8.4.

Table 8.4: Porosity data.

SAMPLE	**Mean bulk density [g/cm^3]**	**Mean absolute gravity [g/cm^3]**	**Porosity Φ**
Gasbeton®	0.515	2.44	0.79
Experimental Cellular Block	0.71	2.43	0.71

8.4.2.3 Microscopic determinations

To further check were made thin sections of the test samples in order to realize the microscopic analysis in plain light with the first filter at 2.5 X and 10 X, with a Zeiss Axioplan Universal Polarizing Microscope.

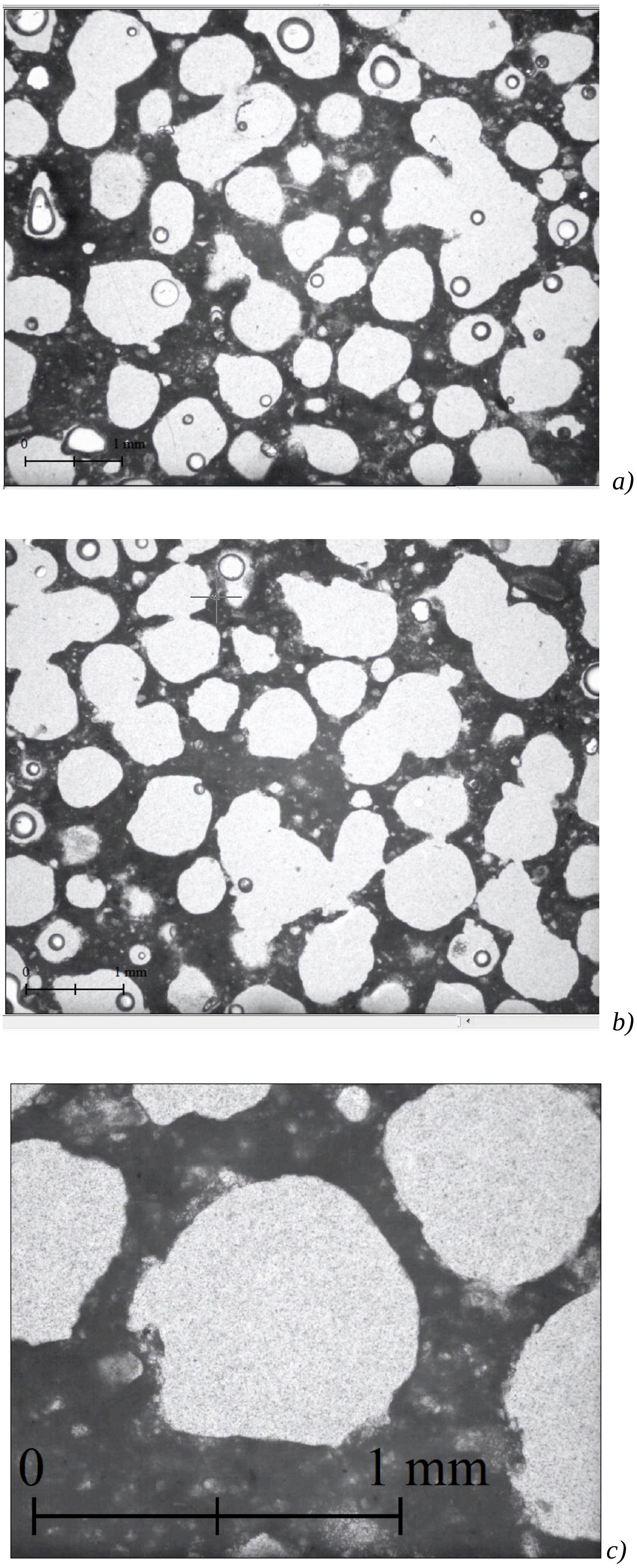

Figure 8.2: a) and b) Gasbeton® sample at 2.5 X. c) Experimental cellular block sample at 10 X.

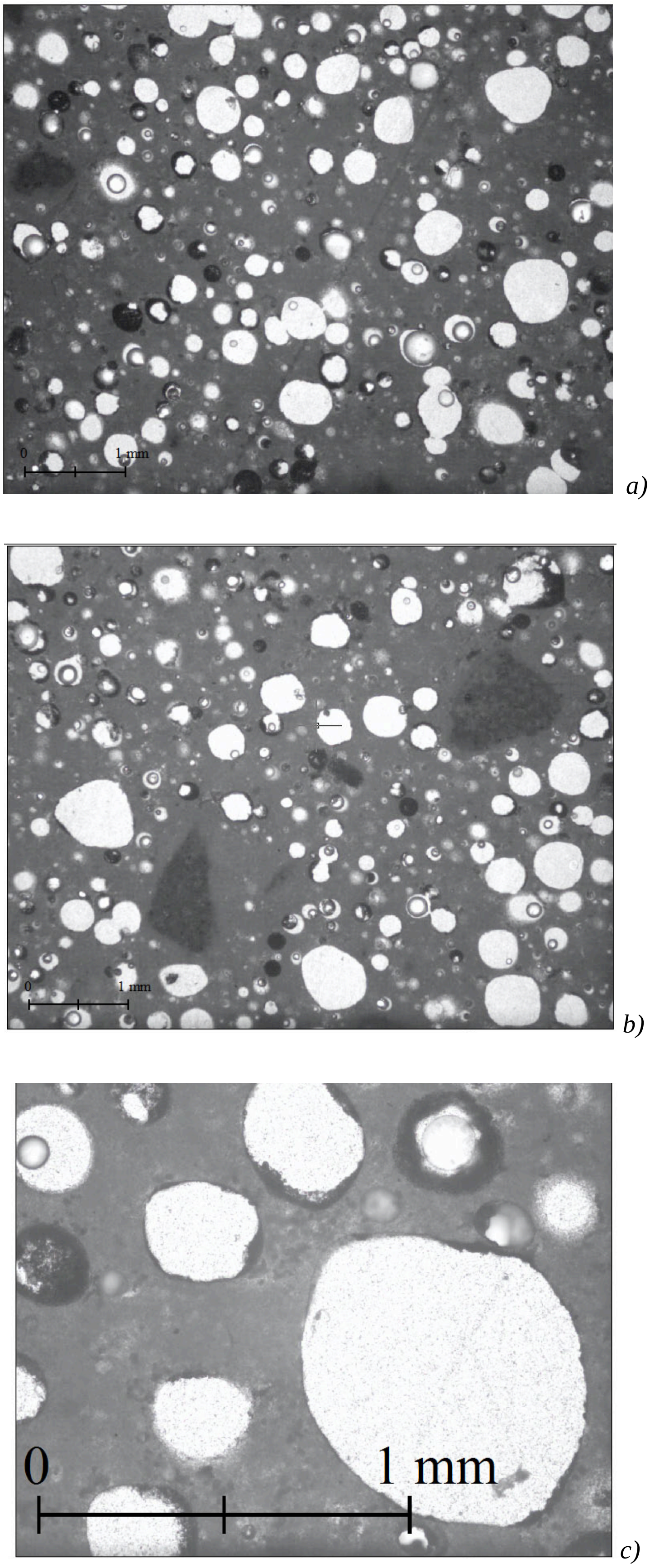

Figure 8.3: a) and b): Experimental cellular block at 2.5 X a 10 X. c) Experimental cellular block at 10 X.

8.4.3 Mineralogical characterization - XRay Diffraction

On two representative samples were carried out mineralogical determination in order to identify the

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

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

The spectra in Fig. 8.4 and Fig. 8.5 illustrate the results of mineralogical analysis.

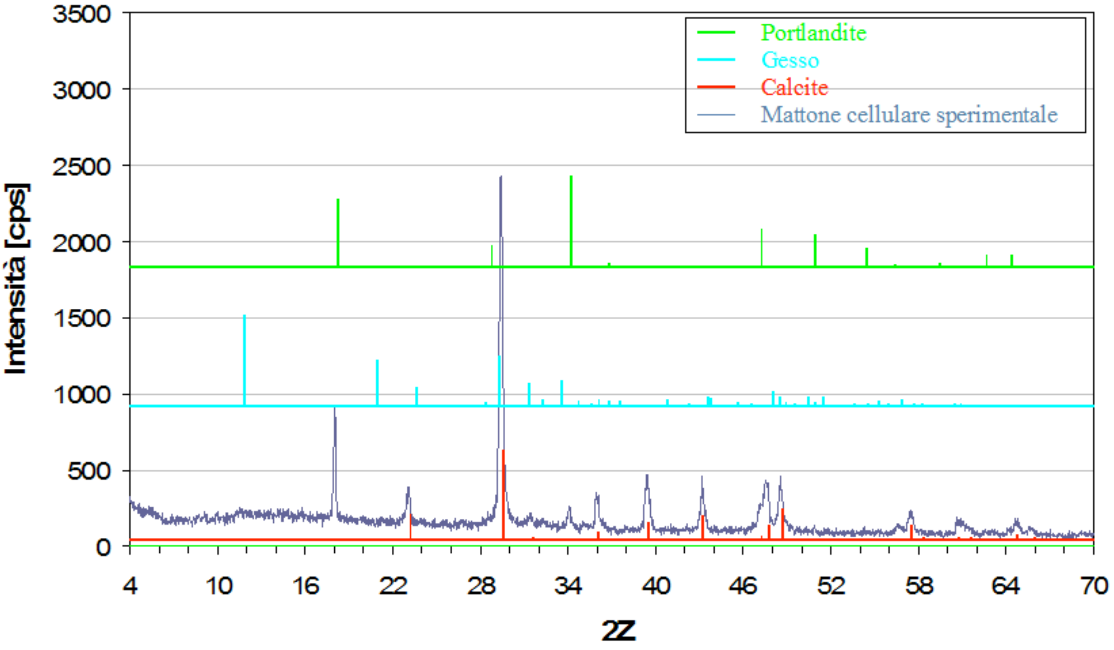

Figure 8.4: Experimental cellular block spectrum.

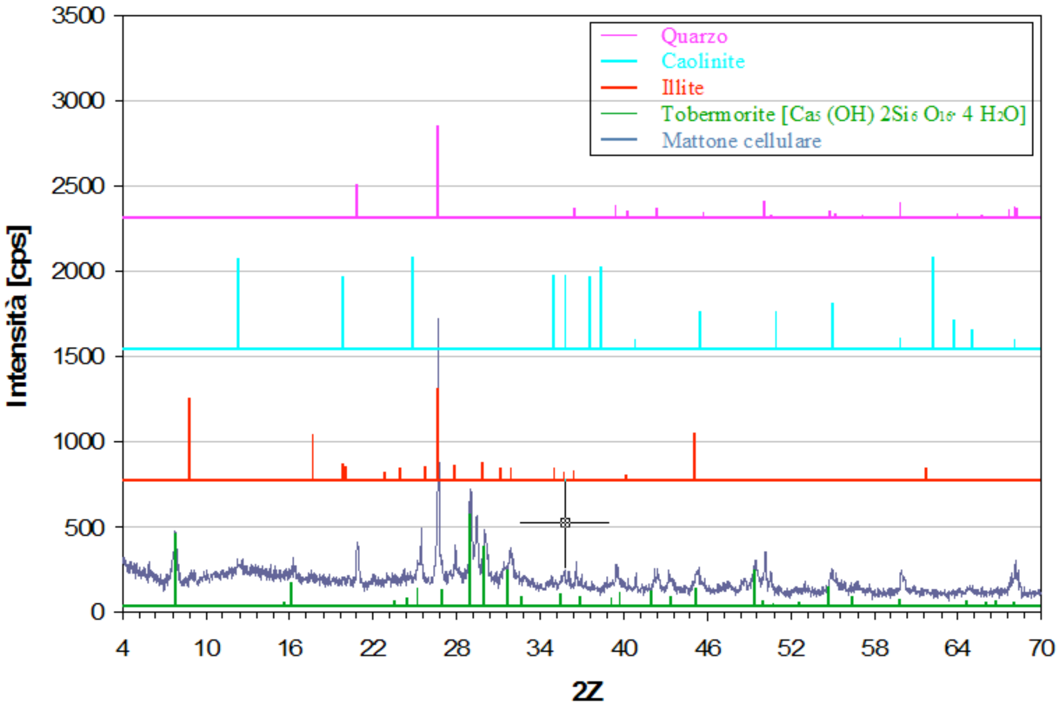

Figure 8.5: Gasbeton® spectrum.

8.5 Results and Discussion

8.5.1 Workability

The dewatered sludge, used in place of the inert classics, has influenced the experimental specimen improving the workability and allowing to obtain homogeneous and quite compact blocks.

8.5.2 Microscopic determinations

As shown in the Figures 8.2 a, b and c the Gasbeton® sample has a homogeneous matrix of dark colour type apparently compact, dense, evenly distributed pores have similar size characteristics of the order of 0.8 mm, the porosity also is generally closed .

With regard to the experimental cellular block, Figures 8.3 a, b and c it can be seen that there is an uneven and porous matrix of light-coloured. The porosity of the sample, closed type, has size ranging between 0.7 mm and 0.25 mm and is unequally distributed in space.

In addition, the experimental cellular blocks have matrix with effective porosity. It is so because past a few hours of sample immersion in the liquid it is fell in the bottom of the cylinder. Not occurred the same for the Gasbeton® sample.

8.5.3 Mineralogical determinations

The graphs illustrates the results of mineralogical analysis: the XRD spectrum in Fig. 8.4 shows that the mineral constituents detected are portlandite, gypsum and calcite.

Instead the Gasbeton® spectrum, Fig. 8.5, shows that the mineral constituents detected are illite, kaolinite, quartz and tobermorite.

8.6 Conclusions

The experiment conducted has shown that it is possible to utilize the sawing marble sludge as a by-product in cellular aggregates production, even if the research was restricted to a no-autoclave study; for this reason it was impossible to study the effect that filter press sludge have in setting, hardening and also for mechanical behaviour.

The entrepreneur with whom this experimental phase was conducted has requested not to explain the mix design of the various blocks until the study will not closed.

Note that using dewatered sludge as aggregate in the mix design reduces water consumption by ensuring the mixture to maintain a good flow and giving the mix a whitish gray colour.

Blocks maturing processes in a not monitored environment causes both the strength decrease and the additive consumption increase than those recommended by the manufacturer.

It was also noted that the sludge percentage variation in mix design didn’t change of the time required for rising; on the contrary time for hardening was increased.

As mentioned above, and as can be imagined, the experimental blocks strength is significantly reduced by increasing content of mud; the product, apparently identical to the one made with lower mud percentages, is very crumbly. This feature makes it impossible cutting processes (by sawing): the saw-plane surfaces are, in fact, irregulars, moreover sawing cause a crumbling of the sample.

It’s certainly possible to increase the resistance both by increasing the cement content and by firing with controlled humidity; unfortunately, due to technical limits, it was possible to verify just that the higher the percentage of concrete, the higher the final product strength. However both lightness and porosity, that are strategic features, will be reduced.

As written before, it is not possible to describe the mix design for the different produced blocks; anyway the following considerations can be drawn:

- The amount of water needed for processing was less than that usually required in mortar mixing, detected in similar tests; this result is justified by the fact that the used sludge has a water content of about 24 %;
- A larger amount of additive was necessary to use with respect on than that recommended by the manufacturer, probably because the paste was not completed on both controlled temperature and humidity;
- Blocks were made by varying the sludge content in mix design from 90% to 70% by weight (remember that the sludge has a certain water content) and it was observed that by percentage increasing:
    - The paste maintained a excellent workability while also reducing demand for water, without undergoing substantial changes in color and maintaining a excellent processability;
    - The required additive amount has not changed
    - The time required for hardening were increased
    - The strength of the cellular blocks is significantly reduced

Nevertheless, as written before, the study is ongoing and needs to be supplemented with autoclave – processes and mechanical studies.

REFERENCES

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Pacenti, V., 1966. “Il Calcestruzzo nell’edilizia moderna, tecnologia ed applicazioni”. Dedalo libri, 1966.

Links

www.gasbeton.it

http://www.glossary.oilfield.slb.com/default.cfm

9. ECONOMY

Calcium carbonate market, especially both in aggregates and fine powder products, has grown considerably over the last 20 years due to increased demand by many industrial sectors described in the thesis.

Three main types of calcium carbonate can be distinguished in the market (Villavecchia and Eigenmann, 1975).

1) Limestone/Calcium carbonate (LCC). It includes marble, hard calcite, and semi-crystalline calcite with a $CaCO_3$ grade of 97 to 99%. Top of impurities are silica, alumina and iron oxide; anyway, only the latter impoverishes the product by altering the whiteness required for many applications. Depending on the particle size, LCC can be used as dimension stone (> 1 m), building stone (> 30 cm), aggregates (1 – 20 cm), chemicals and glass (0.2 – 5 cm), filter bed stone, poultry grit (3 - 8 cm), foundry and fluxstone (< 3 cm), filler, mild abrasive, glazes and enamels, mine dust, fungicide and insecticide carrier (< 0.2 mm), reagent (< 1 mm).

2) Ground Calcium carbonate (GCC). It is excavated from surface deposits having amorphous and friable structure, consisting mainly of foraminifera and polluted by silica. Wet separation is appropriately replaced by the dry one and classification, especially in industrial applications characterised by of high whiteness grade. The $CaCO_3$ grade runs from 95 to 99%; impurities are around 0.70% silica, 0.40% iron oxide and 0.30% alumina. It is widely used as a filler in manufactured products ranging from asphalt to art paper.

3) Precipitated Calcium carbonate (PCC). It is obtained by milk of lime precipitation by carbon dioxide and as a by-product from the production of ammonium sulphate from gypsum. PCC is whiter and purer than the natural Calcium carbonate. It is used in filler and coater in paper, filler in plastics paints and coatings, elastomers, food, drugs and pharmaceuticals.

It is noteworthy that the pure carbonates, compared with limestones, have a high market value (160 ÷ 220 €/t) due to their purity (high $CaCO_3$ grade, more than 99.5%).

In addition to purity, as can be seen in the chart shown in figure (XY), the market value of the Calcium carbonate also varies as a function of particle size in which it is sold.

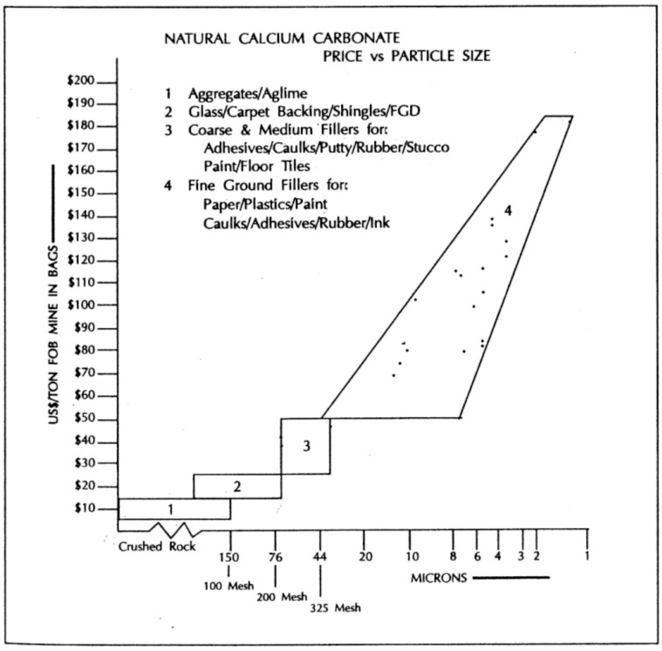

Figure 9.1: Natural Calcium carbonate price related with Particle Size (Harben, P. W., 1995).

Current prices for LCC, GCC and PCC products FOB works and bagged are summarized in the Tables 9.1, 9.2, 9.3.

Table 9.1: LCC

GRADE	Mean particle size [mm]	FOB price [€/t]
Aggregate/aglime[2]	10 – 200	3 – 8
Glass grade	0,074 – 0,15	11 - 22
Screened product		44 -55 (bulk) 60 – 70 (bags)
Coarse grind		26 – 33 (rock dust, bulk) 30 - 37 (industriall filler, bulk) 37 – 44 (industrial filler, bags)
Medium grind		26 – 44 (bulk) 33 – 55 (bags)

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[2] **Aglime** is crushed limestone or dolomite used for soil treatment, primarily to reduce soil acidity.

Table 9.2: GCC

GRADE	Mean particle size [μm]	Top size [μm]	FOB price, bagged [€/t]
Dry, coarse	9 - 17	40 - 80	70 - 100
Dry, medium	4 – 9	15 - 35	56 - 91
Dry - fine	0.5	5	100 - 112
Coated, fine	2 - 3	10	150 - 176
Coated, ultrafine	1	5	213

Table 9.3: PCC

GRADE	Mean particle size [μm]	FOB price, bagged [€/t]
Technical	0.5	198 - 210
Ultrafine	0.05 – 0.5	465

Based on these data, it's possible to estimate a selling price of sawing dust produced in the marble area of Orosei equal to:

- 80 €/t for particle mean sizes of 10 μm to 100 μm;
- 150 €/t for particle mean sizes < 10 μm;

About 300,000 m^3 gangsaw blocks are annually quarried in the marble area mentioned, half of which are sent directly to the sawing plants for the slabs production (the remaining half is instead sold). Slabs then undergo further processing (cutting, bush-hammering, honing/polishing, finishing) until obtaining the final product.

Thus about 40% of the processed stone is reduced to fine powders that form the sludge from which are extracted through filter press, the dewaterd dust.

From a quick calculation it can say that about 60,000 m^3 of dust are generated every year; this amount is currently allocated in the municipal landfill.

The analysis carried out in the thesis show that, on average, 72% of the dewaterd sludge, taken from the filter press, has a particle size less than 10 microns. It is therefore possible to envisage a preliminary economic evaluation by knowing the amount of fine material for sale, differentiated by size fraction. The table 9.4 summarizes these evaluations.

Table 9.4:Experimental evaluation.

Total annual amount of dust [m^3]	**Amount of dust distributed to size fractions [m^3]**	**Unit weigth [t/m^3]**	**Annual amount available for sale [t]**	**Unit price [€/t]**	**Revenues [k€]**	**Total annual revenue [k€]**
60,000	72 % (< 10 μm) 43,200	1.6	69,120	150	10,368	12,518,4
	28 % (> 10 μm) 16,800	1.6	26,880	80	2,140.4	

From the table 9.4, it is clear the economic advantage in the marketing of dewatered sludge as a byproduct. The annual revenue related to this transaction would exceed the 12 M€, which is equal to the turnover of two medium-sized companies in dimension stone sector. This would result in a significant contribution to the completion of the supply chain of the Orosei marble production industry, connected to the real possibility of increased employment and to a significant increase in the value added of vertical production chain of stone quarrying, sawing and processing.

Note that in addition to these revenues should be also taken into account savings related to elimination of the haulage costs of dewatered sludge in municipal landfill.

It’s also to be kept on mind that the industrial marble area of Orosei is strategic from the standpoint of economic and social mostly for the whole Bassa Baronia region and fairly important for the province of Nuoro; the activation of this new sector of recovery, processing and marketing of limestone fine dust will have considerable economic benefits for both the province and region.

It is also conceivable, with continued research, to further improve the material properties of dewatered sludge, through appropriate treatment processes. In this way it will better meet the requirements of $CaCO_3$ on industrial sectors, albeit with an increase in the sales price.

It is also conceivable, with continued research, to further improve the material properties of dewatered sludge, through appropriate treatment processes. In this way it will better meet the requirements of $CaCO_3$ of different industrial sectors, albeit with an increase in the sales price.

Obviously, to make new investments it is required; they should be carried out by primarily of new plants and equipment, which could also use the financial benefits associated with P.O.R. plans of Regione Sardegna and that, if carried out by a consortium of companies, would be sufficiently guaranteed with regard to capital risk.

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Villavecchia, V., Eigenmann, G., 1975. “Nuovo dizionario di merceologia e chimica applicata”. Ulrico Hoepli Editors Spa. Milano (Italy). Re-printed 1997. ISBN: 88-203-0532-1.

CONCLUSION

The results presented and discussed along this work have shown the necessity of reducing the burden of the waste management, avoiding the negative impact associated with landfill, and of preserving natural resources, for example, by reusing industrial residues, should be regarded as a challenge and a great opportunity to suitably reformulate the traditional building products and keep or even improve their properties.

Nowadays, landfill is the actual main destination for rock residues. By considering the point of view of waste – reuse it is important to underline that recycling has a large number of benefits which have made it a more attractive option in this period of greater environmental awareness, more environmental laws.

What this indicates is the important that research have in the waste – reuse, from the point of view of environmental aspects, and the sustainable development, since the use of waste products from industrial processes reduces the environmental impact of the new material or product, and from a financial standpoint, in connection with the potential cost savings on treatment or disposal of those waste products.

Several companies become to understand the importance of *research and development*. It's clear that this concept is linked with the *innovation* and consequently, with the concept of *sustainable development* and at the light of the entrepreneurs try to recognize and exploit the different opportunities that arise from this concept of research and technology.

All over the world, the ornamental stone industries create vast amount of by-product rock waste that could be used in building production and in particular the rock powder might be suitable to be used in civil engineering construction purposes. As known, the civil engineering construction industry is believed to be one of the most potential consumers of mineral resource, therefore, generating a great amount of solid waste as a by-product.

The research and the experimentation have confirmed the feasibility of exploitation of sludge deriving from marble processing plants and in particular at the end of the waste-water treatment cycle. Until now, the fines shall be considered as an expensive item as waste products to be delivered to approved landfills. Thereby, this work was focused on the valorization of wastes of calcium carbonate from natural stones through its incorporation as alternative raw materials in manufacturing formulations.

The marble dust, sampled in the five plants studied, was tested by performing mineralogical, chemical and physical analysis to identify the absence of pollutants, thus confirming that it could be used in commercial applications and can be economically exploited as by-product for many different industrial processes, involving several sectors. Its strengths are here summarized:

- The high calcium carbonate content;
- The absence of heavy metals and pollutants;
- The particle size with high percentages of ultrafines.

Currently, this waste have a great potential, regarding not only building sector but also pharmaceutical and chemical industries, manufacturing of paper and paints, agriculture and it’s also used in production of rubber and tires.

In this Ph.D. thesis, the properties of waste marble mixes were investigated and were compared with control mix specimen properties. Exploring the following industrial fields:

- Concrete production;
- Brick making;
- Plaster industry;
- Autoclaved aerated concrete manufacturing.

The main result obtained in this dissertation has shown that marble process residues could be used in several industrial field without any previous treatment. What’s more, the outcome presented in the dissertation, shows the feasibility of using this by-product in the mix composition of concrete, bricks, gypsum plaster and autoclaved aerated concrete. According to this research, marble dust should be recycled as partial substitute of paste components.

This means that these inexpensive residues can be regarded as good substitutes for the costly raw materials, therefore preserving the mineral resources, while lowering the production costs.

Looking into the research from economic point of view, thanks to the marketing of marble dust companies, the economy can further improve, in fact it can be noticed that the final products consume large amount of raw materials, in addition to its benefits in saving landscape as well as natural resources, it can be, obviously, cheaper then commercial products.

Despite that, to effectively utilize of these wastes as raw material, filler, binder and additive in developing alternative building materials, detailed physical and chemical engineering, thermal, mineralogical and morphological properties of these wastes are to be evaluated and accurate data made available. In order to maximize the use of alternative building materials developed from different types of solid wastes and to increase the production capacity of lab scale processes, technology-enabling centers are needed to be set up in order to facilitate entrepreneurs for effective commercialization. Durability and performance of the newer products and dissemination of technologies emphasizing costs-benefits analyses and life cycle assessment report will significantly contribute to successful commercialization of innovative processes. Inclusion of industrial waste-based newer building materials will give fillip to such technology promotion.

The scientific advancement in recycling and using industrial processes for utilizing wastes will lead to a better use of world’s resources. The endeavour, therefore, needs to be to encourage entrepreneurs and construction agencies to develop new products and processes using all these wastes as raw materials for setting up secondary industries and contributing to reduction of green house gases and global warming. However, difficult the task is o may be, we can't give up.

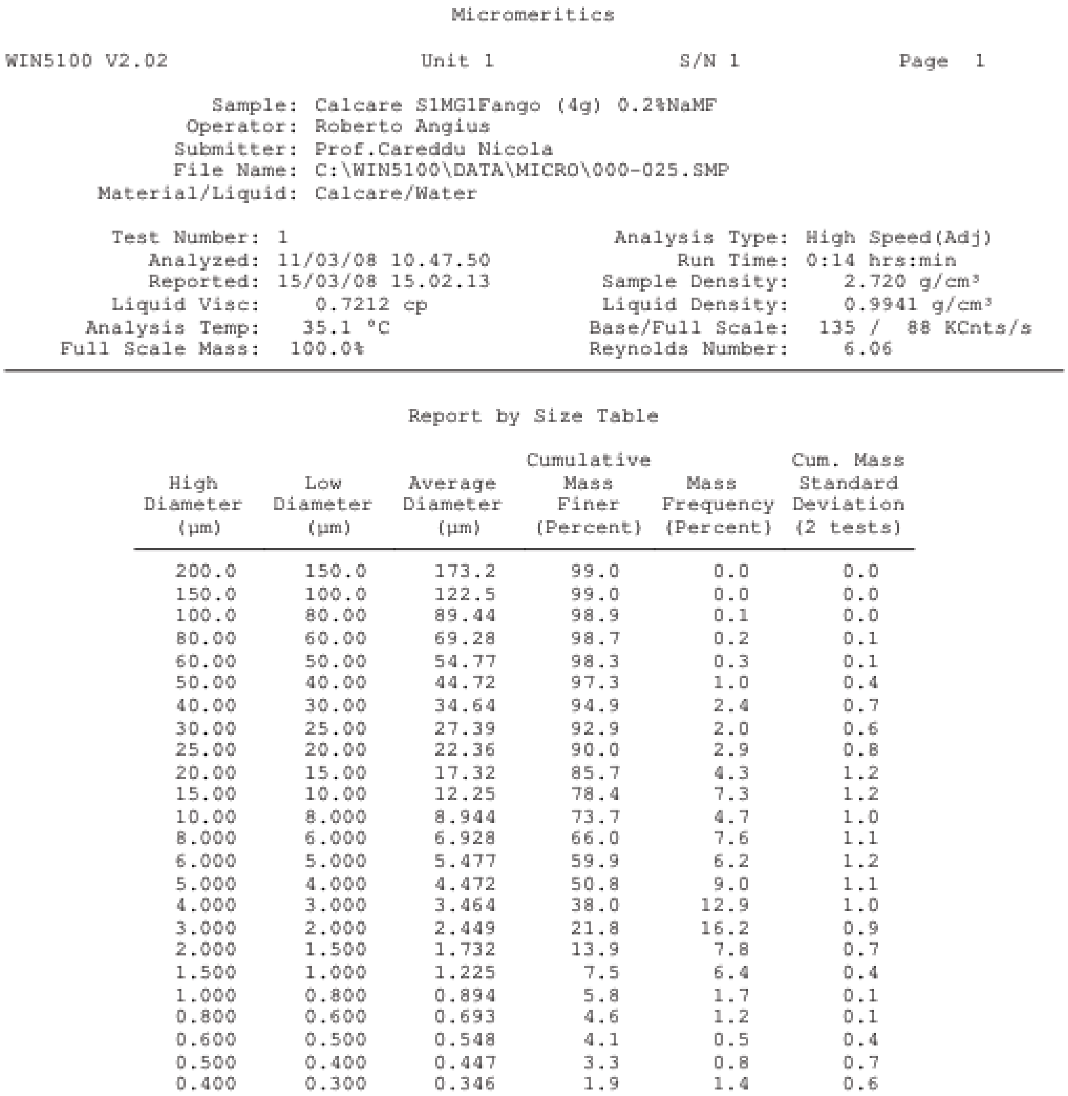
Summarizing, the results, presented in the doctoral thesis, enable to draw the following general conclusions:

- Using recycled material reduces the need for exploiting
- Residues can be regarded as good substitutes for the costly raw materials
- Waste reuse lessen waste generation and disposal in landfill.

In conclusion, by considering the added value of the waste products generated by dimension stone sawing and processing, future research directions will aim to enhance the quality of the fine material in industrial field applications. So what until now was considered as a waste, really is an important economic resource capable of promoting the sustainable construction.

APPENDIX 1

1.A
SIMG$_1$



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                              Micromeritics

WIN5100 V2.02                   Unit 1             S/N 1           Page  1

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            Operator: Roberto Angius
           Submitter: Prof.Careddu Nicola
           File Name: C:\WIN5100\DATA\MICRO\000-025.SMP
      Material/Liquid: Calcare/Water

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      Liquid Visc:    0.7212 cp             Liquid Density:    0.9941 g/cm³
    Analysis Temp:   35.1 °C              Base/Full Scale:  135 /  88 KCnts/s
  Full Scale Mass:  100.0%                Reynolds Number:    6.06
___________________________________________________________________________

                            Report by Size Table

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           High       Low    Average   Mass      Mass     Standard
        Diameter   Diameter  Diameter  Finer   Frequency  Deviation
          (µm)       (µm)      (µm)   (Percent) (Percent) (2 tests)
        ____________________________________________________________
          200.0     150.0     173.2     99.0      0.0       0.0
          150.0     100.0     122.5     99.0      0.0       0.0
          100.0     80.00     89.44     98.9      0.1       0.0
          80.00     60.00     69.28     98.7      0.2       0.1
          60.00     50.00     54.77     98.3      0.3       0.1
          50.00     40.00     44.72     97.3      1.0       0.4
          40.00     30.00     34.64     94.9      2.4       0.7
          30.00     25.00     27.39     92.9      2.0       0.6
          25.00     20.00     22.36     90.0      2.9       0.8
          20.00     15.00     17.32     85.7      4.3       1.2
          15.00     10.00     12.25     78.4      7.3       1.2
          10.00     8.000     8.944     73.7      4.7       1.0
          8.000     6.000     6.928     66.0      7.6       1.1
          6.000     5.000     5.477     59.9      6.2       1.2
          5.000     4.000     4.472     50.8      9.0       1.1
          4.000     3.000     3.464     38.0     12.9       1.0
          3.000     2.000     2.449     21.8     16.2       0.9
          2.000     1.500     1.732     13.9      7.8       0.7
          1.500     1.000     1.225      7.5      6.4       0.4
          1.000     0.800     0.894      5.8      1.7       0.1
          0.800     0.600     0.693      4.6      1.2       0.1
          0.600     0.500     0.548      4.1      0.5       0.4
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          0.400     0.300     0.346      1.9      1.4       0.6
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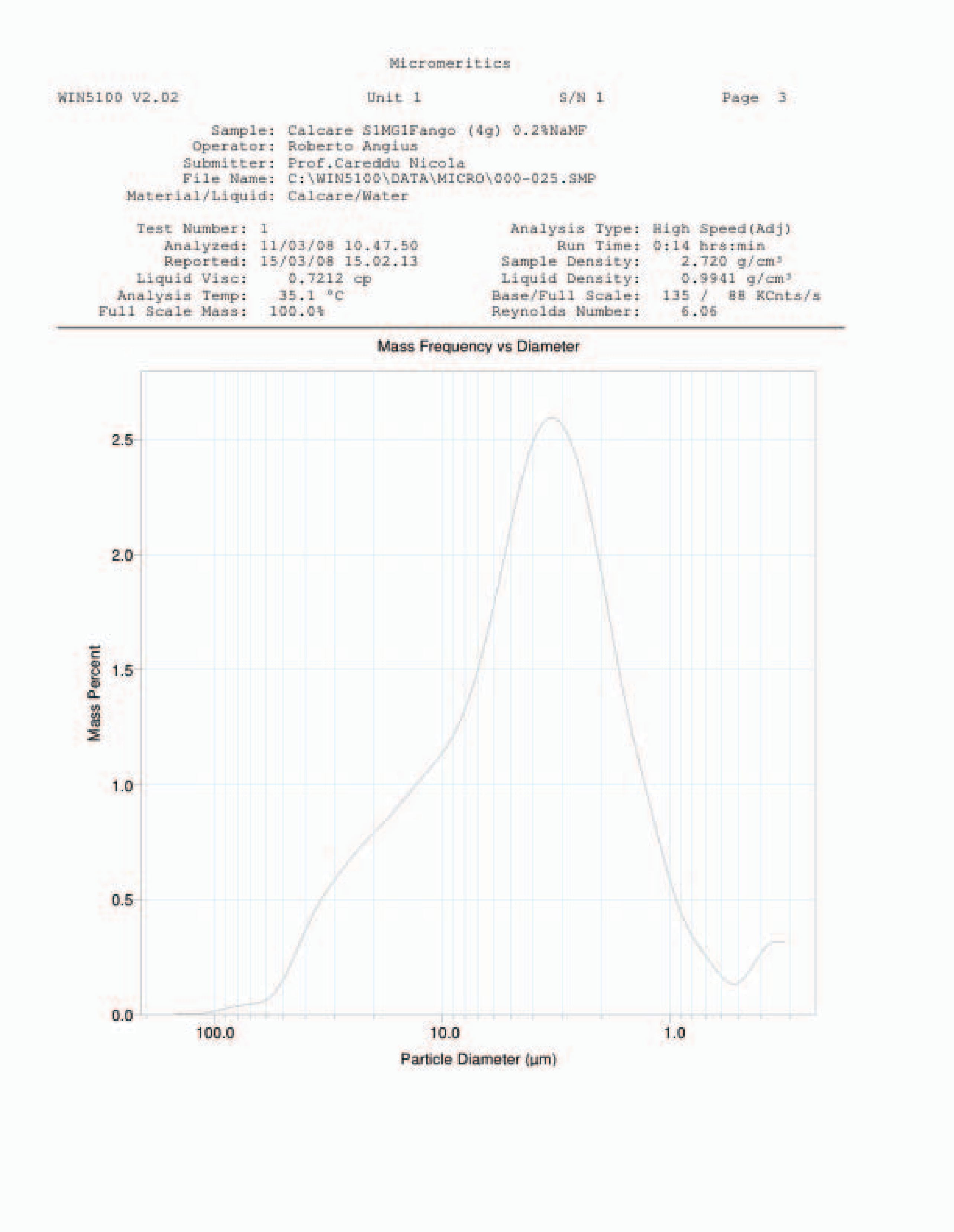

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        Submitter: Prof.Careddu Nicola
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     Liquid Visc:     0.7212 cp            Liquid Density:    0.9941 g/cm³
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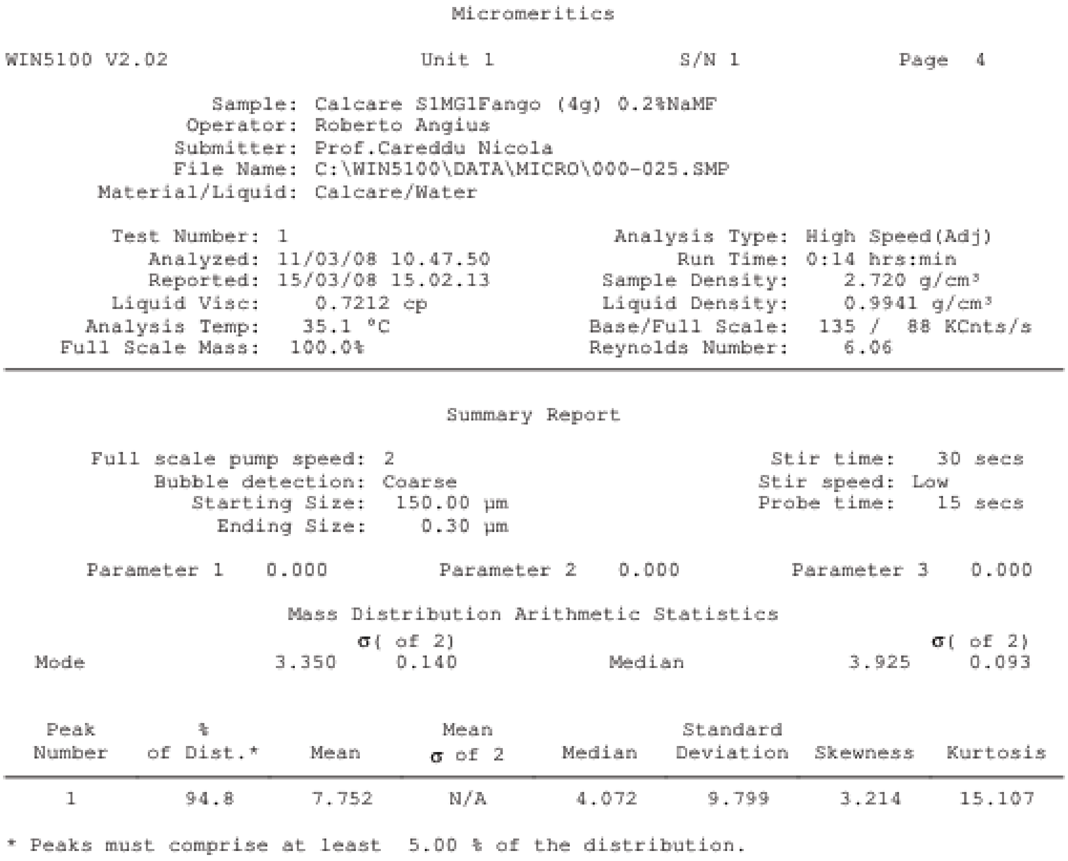

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           Reported: 15/03/08 15.02.13    Sample Density:    2.720 g/cm³
        Liquid Visc:    0.7212 cp         Liquid Density:    0.9941 g/cm³
      Analysis Temp:   35.1 °C           Base/Full Scale:  135 /  88 KCnts/s
    Full Scale Mass:  100.0%             Reynolds Number:    6.06

                                 Summary Report

      Full scale pump speed: 2                             Stir time:   30 secs
           Bubble detection: Coarse                       Stir speed: Low
              Starting Size:  150.00 µm                   Probe time:   15 secs
                Ending Size:    0.30 µm

      Parameter 1   0.000        Parameter 2   0.000        Parameter 3   0.000

                        Mass Distribution Arithmetic Statistics
                             σ( of 2)                                   σ( of 2)
  Mode                3.350     0.140          Median            3.925     0.093

  Peak        %                     Mean              Standard
 Number   of Dist.*     Mean       σ of 2     Median   Deviation  Skewness  Kurtosis

    1        94.8       7.752       N/A       4.072      9.799      3.214    15.107

* Peaks must comprise at least  5.00 % of the distribution.
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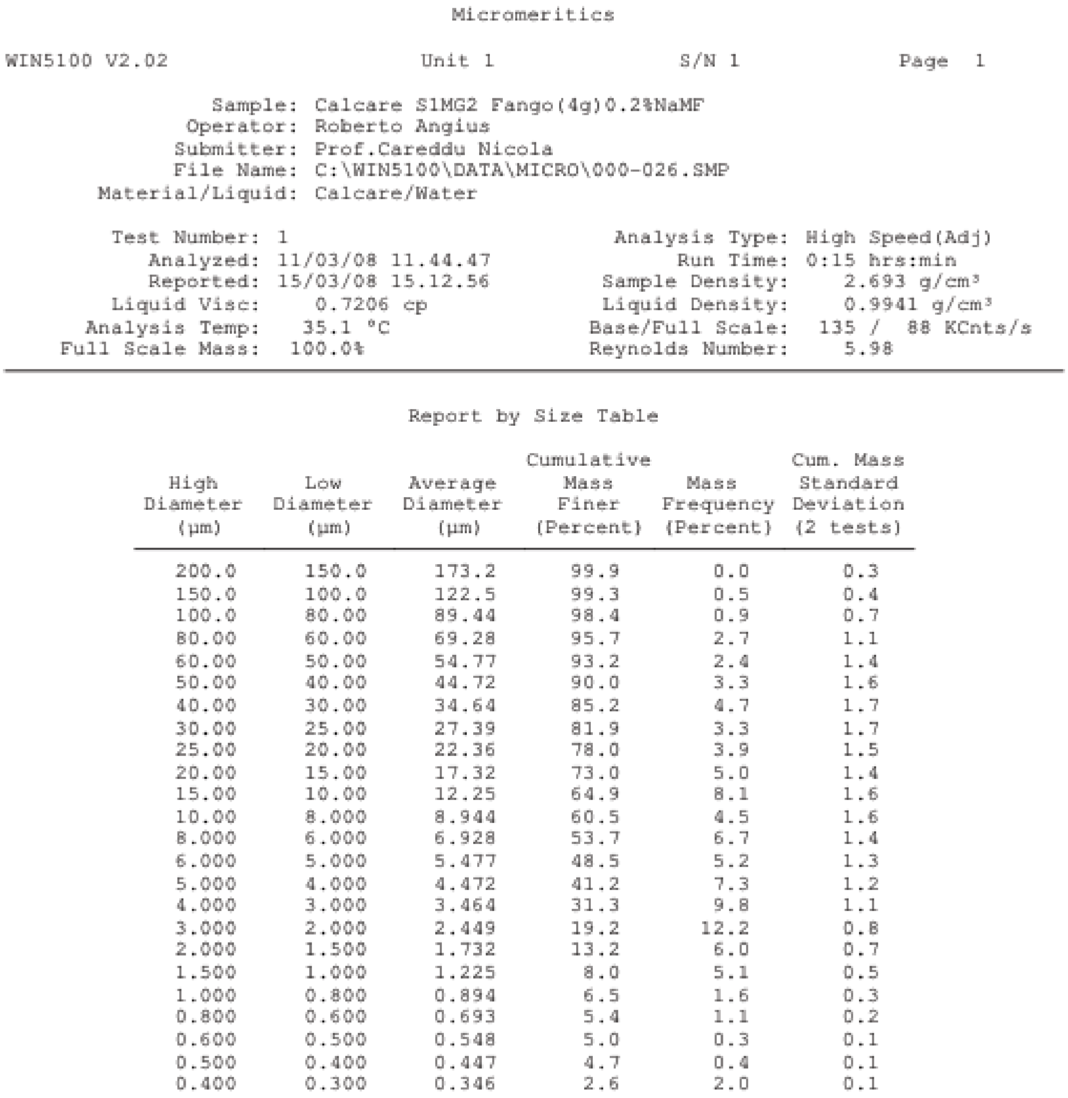
1.B
SIMG$_2$



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                              Micromeritics

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          Submitter: Prof.Careddu Nicola
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     Material/Liquid: Calcare/Water

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                            Report by Size Table

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       Diameter  Diameter   Diameter    Finer   Frequency  Deviation
          (µm)      (µm)       (µm)   (Percent) (Percent)  (2 tests)

          200.0     150.0      173.2     99.9       0.0        0.3
          150.0     100.0      122.5     99.3       0.5        0.4
          100.0     80.00      89.44     98.4       0.9        0.7
          80.00     60.00      69.28     95.7       2.7        1.1
          60.00     50.00      54.77     93.2       2.4        1.4
          50.00     40.00      44.72     90.0       3.3        1.6
          40.00     30.00      34.64     85.2       4.7        1.7
          30.00     25.00      27.39     81.9       3.3        1.7
          25.00     20.00      22.36     78.0       3.9        1.5
          20.00     15.00      17.32     73.0       5.0        1.4
          15.00     10.00      12.25     64.9       8.1        1.6
          10.00     8.000      8.944     60.5       4.5        1.6
          8.000     6.000      6.928     53.7       6.7        1.4
          6.000     5.000      5.477     48.5       5.2        1.3
          5.000     4.000      4.472     41.2       7.3        1.2
          4.000     3.000      3.464     31.3       9.8        1.1
          3.000     2.000      2.449     19.2      12.2        0.8
          2.000     1.500      1.732     13.2       6.0        0.7
          1.500     1.000      1.225      8.0       5.1        0.5
          1.000     0.800      0.894      6.5       1.6        0.3
          0.800     0.600      0.693      5.4       1.1        0.2
          0.600     0.500      0.548      5.0       0.3        0.1
          0.500     0.400      0.447      4.7       0.4        0.1
          0.400     0.300      0.346      2.6       2.0        0.1
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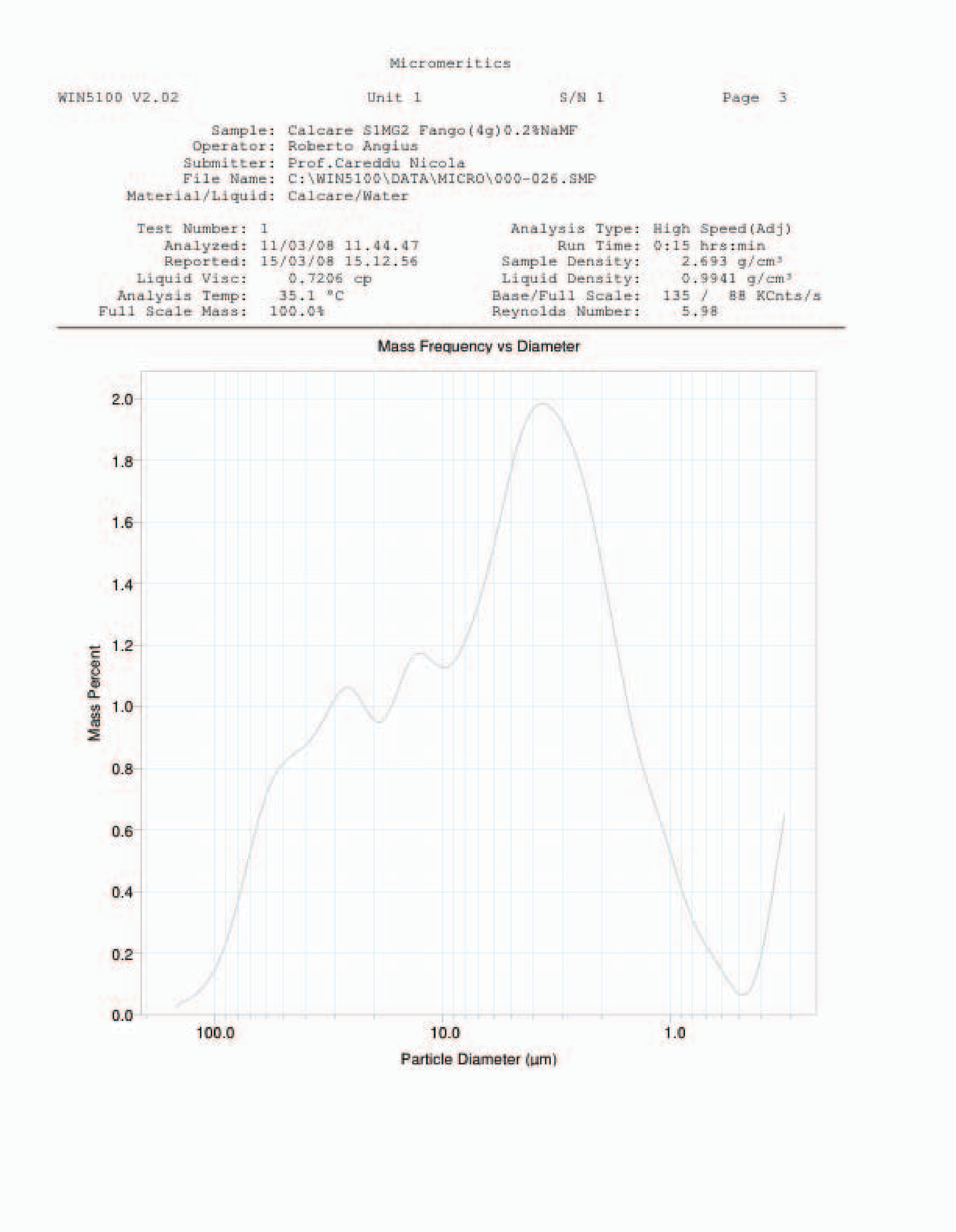

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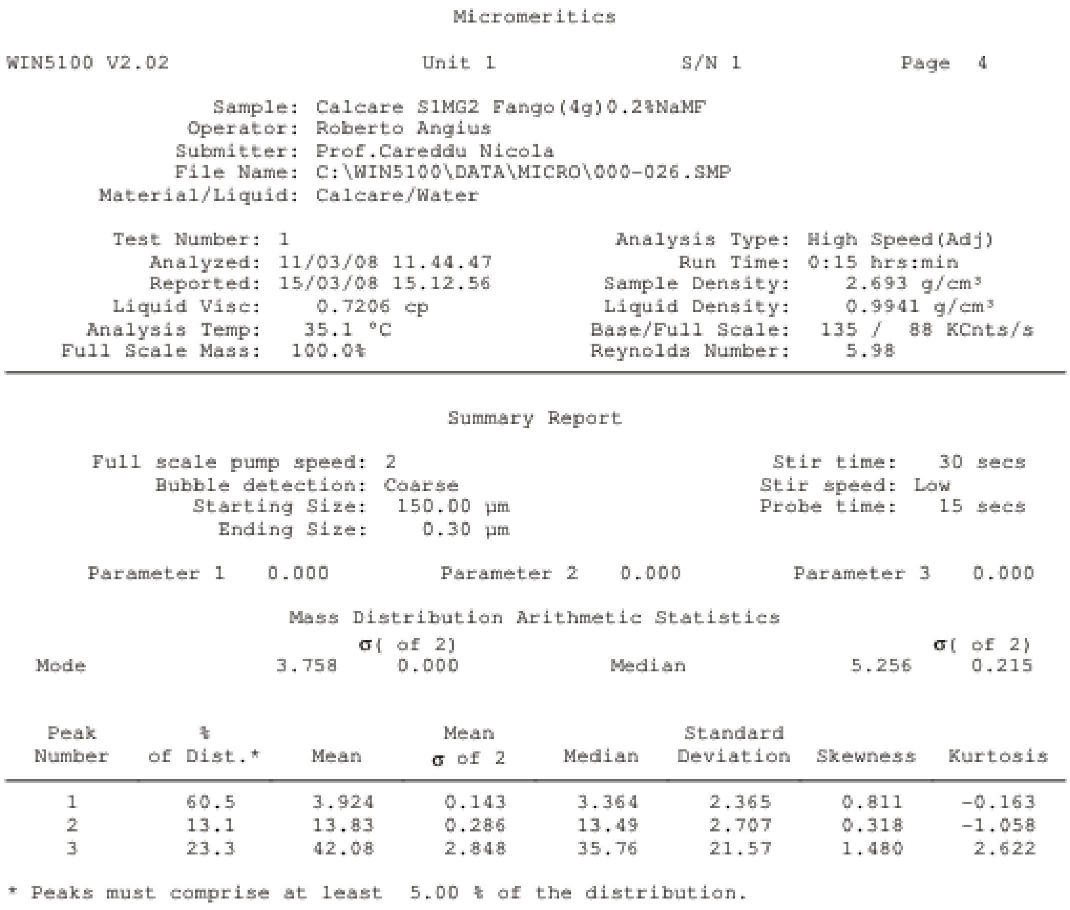
             Operator:  Roberto Angius
            Submitter:  Prof.Careddu Nicola
            File Name:  C:\WIN5100\DATA\MICRO\000-026.SMP
       Material/Liquid:  Calcare/Water

        Test Number:  1                          Analysis Type:  High Speed(Adj)
           Analyzed:  11/03/08 11.44.47               Run Time:  0:15 hrs:min
           Reported:  15/03/08 15.12.56           Sample Density:     2.693 g/cm³
        Liquid Visc:     0.7206 cp                Liquid Density:     0.9941 g/cm³
      Analysis Temp:    35.1 °C                  Base/Full Scale:  135 /  88 KCnts/s
    Full Scale Mass:   100.0%                   Reynolds Number:     5.98
```

Mass Frequency vs Diameter



```
                                      Micromeritics

WIN5100 V2.02                   Unit 1              S/N 1            Page  4

                  Sample: Calcare S1MG2 Fango(4g)0.2%NaMF
                Operator: Roberto Angius
               Submitter: Prof.Careddu Nicola
               File Name: C:\WIN5100\DATA\MICRO\000-026.SMP
          Material/Liquid: Calcare/Water

        Test Number: 1                          Analysis Type: High Speed(Adj)
           Analyzed: 11/03/08 11.44.47               Run Time: 0:15 hrs:min
           Reported: 15/03/08 15.12.56         Sample Density:    2.693 g/cm³
        Liquid Visc:     0.7206 cp             Liquid Density:    0.9941 g/cm³
      Analysis Temp:    35.1 °C              Base/Full Scale:  135 /  88 KCnts/s
    Full Scale Mass:  100.0%                 Reynolds Number:     5.98
_____________________________________________________________________________________

                                      Summary Report

      Full scale pump speed: 2                                Stir time:   30 secs
           Bubble detection: Coarse                          Stir speed: Low
              Starting Size:  150.00 µm                      Probe time:   15 secs
                Ending Size:    0.30 µm

      Parameter 1    0.000         Parameter 2    0.000         Parameter 3    0.000

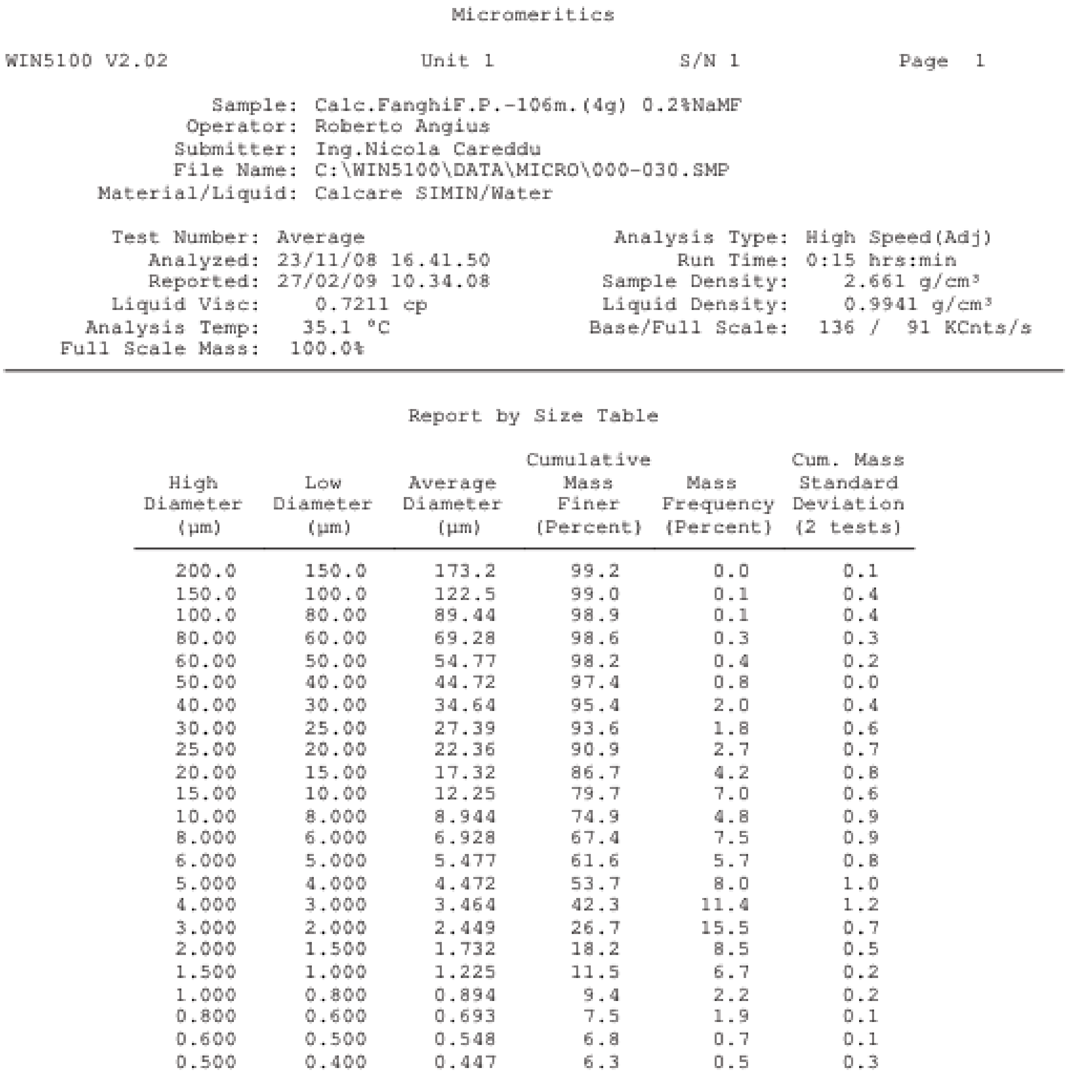
                          Mass Distribution Arithmetic Statistics
                               σ( of 2)                                         σ( of 2)
  Mode                 3.758     0.000          Median               5.256     0.215

  Peak        %                     Mean                  Standard
 Number   of Dist.*     Mean      σ of 2      Median     Deviation   Skewness   Kurtosis
_____________________________________________________________________________________

    1        60.5       3.924      0.143       3.364       2.365       0.811     -0.163
    2        13.1       13.83      0.286       13.49       2.707       0.318     -1.058
    3        23.3       42.08      2.848       35.76       21.57       1.480      2.622

* Peaks must comprise at least  5.00 % of the distribution.
```

1.C
SIMIN



```
                               Micromeritics

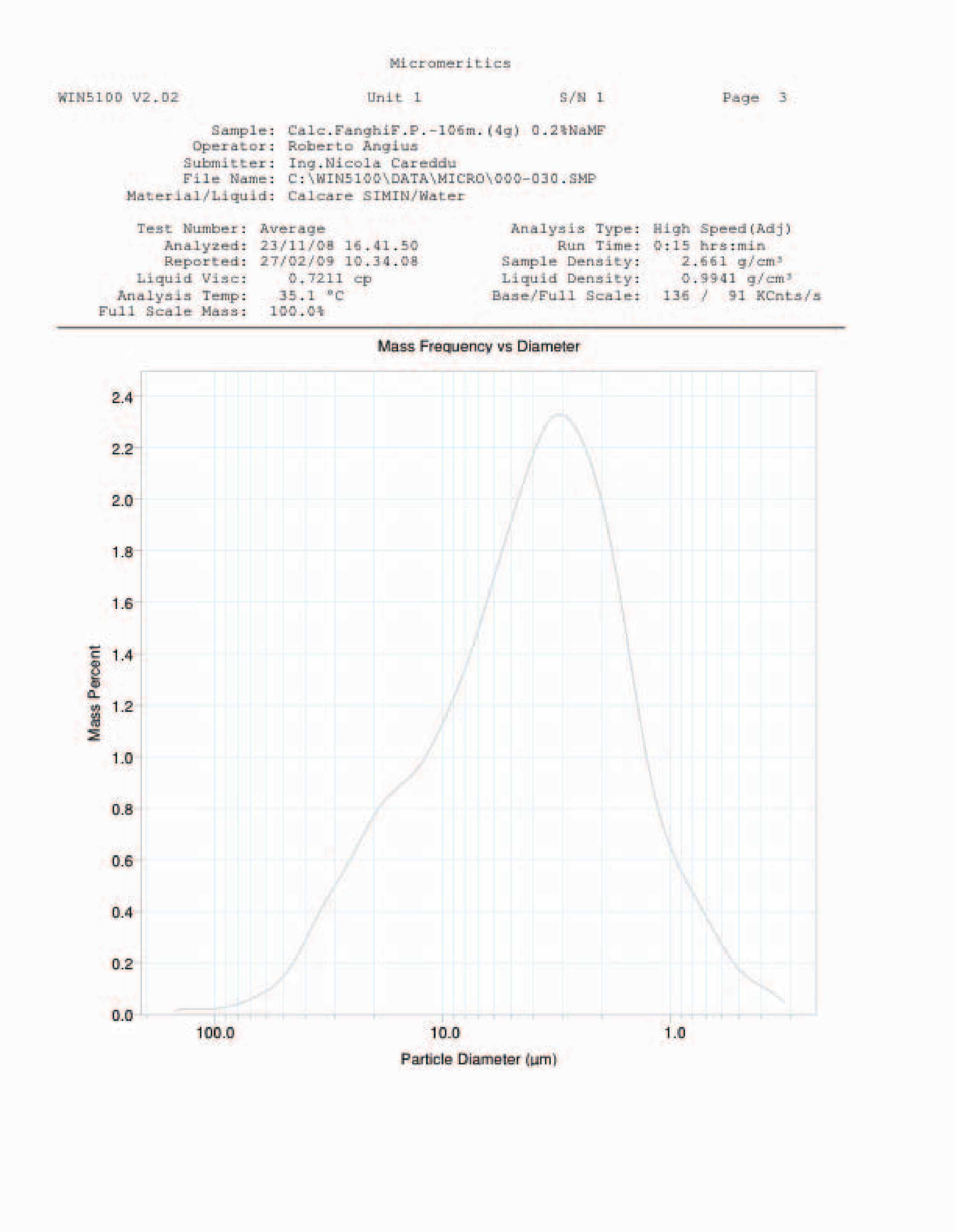
WIN5100 V2.02                  Unit 1             S/N 1           Page  1

               Sample:  Calc.FanghiF.P.-106m.(4g) 0.2%NaMF
             Operator:  Roberto Angius
            Submitter:  Ing.Nicola Careddu
            File Name:  C:\WIN5100\DATA\MICRO\000-030.SMP
       Material/Liquid:  Calcare SIMIN/Water

        Test Number:  Average                  Analysis Type:  High Speed(Adj)
           Analyzed:  23/11/08 16.41.50             Run Time:  0:15 hrs:min
           Reported:  27/02/09 10.34.08       Sample Density:     2.661 g/cm³
        Liquid Visc:     0.7211 cp            Liquid Density:     0.9941 g/cm³
      Analysis Temp:    35.1 °C              Base/Full Scale:   136 /  91 KCnts/s
    Full Scale Mass:   100.0%
______________________________________________________________________________

                           Report by Size Table

                                     Cumulative             Cum. Mass
             High       Low      Average      Mass      Mass     Standard
           Diameter   Diameter   Diameter    Finer    Frequency  Deviation
             (µm)       (µm)       (µm)    (Percent)  (Percent)  (2 tests)
          _________________________________________________________________
            200.0      150.0      173.2      99.2       0.0        0.1
            150.0      100.0      122.5      99.0       0.1        0.4
            100.0      80.00      89.44      98.9       0.1        0.4
            80.00      60.00      69.28      98.6       0.3        0.3
            60.00      50.00      54.77      98.2       0.4        0.2
            50.00      40.00      44.72      97.4       0.8        0.0
            40.00      30.00      34.64      95.4       2.0        0.4
            30.00      25.00      27.39      93.6       1.8        0.6
            25.00      20.00      22.36      90.9       2.7        0.7
            20.00      15.00      17.32      86.7       4.2        0.8
            15.00      10.00      12.25      79.7       7.0        0.6
            10.00      8.000      8.944      74.9       4.8        0.9
            8.000      6.000      6.928      67.4       7.5        0.9
            6.000      5.000      5.477      61.6       5.7        0.8
            5.000      4.000      4.472      53.7       8.0        1.0
            4.000      3.000      3.464      42.3      11.4        1.2
            3.000      2.000      2.449      26.7      15.5        0.7
            2.000      1.500      1.732      18.2       8.5        0.5
            1.500      1.000      1.225      11.5       6.7        0.2
            1.000      0.800      0.894       9.4       2.2        0.2
            0.800      0.600      0.693       7.5       1.9        0.1
            0.600      0.500      0.548       6.8       0.7        0.1
            0.500      0.400      0.447       6.3       0.5        0.3
```

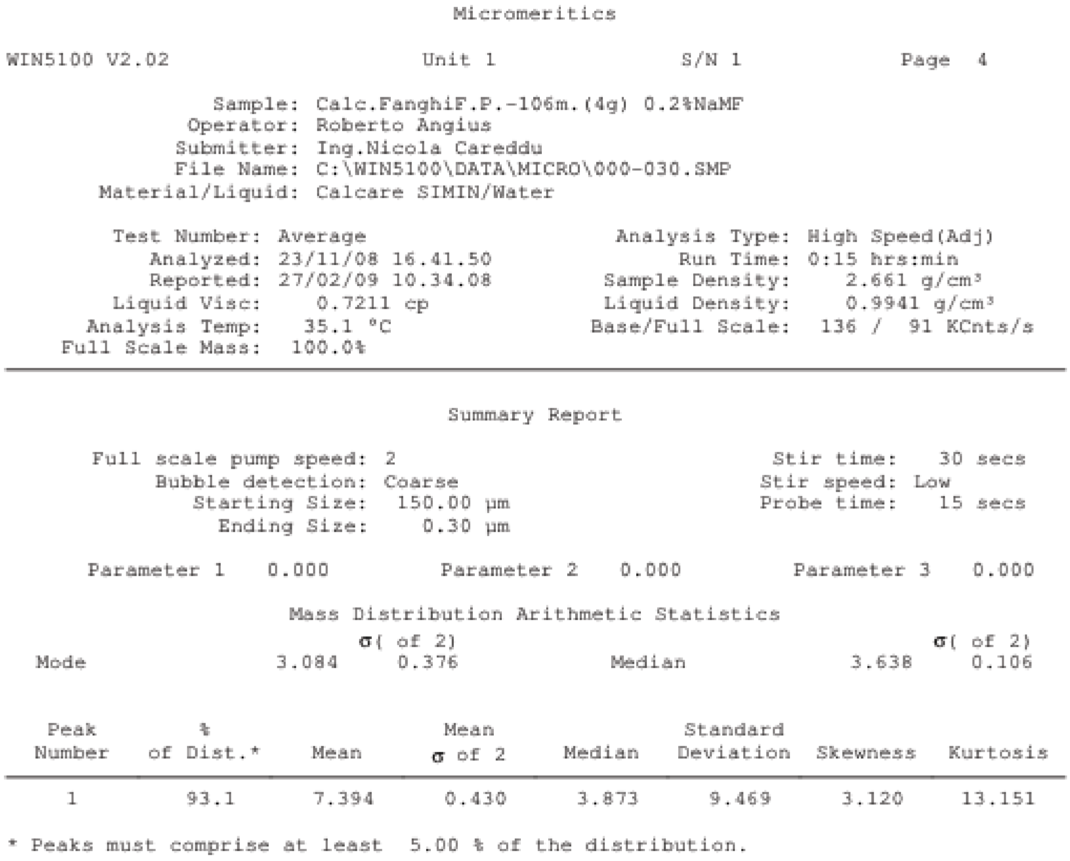


```
                              Micromeritics

WIN5100 V2.02                    Unit 1             S/N 1           Page  3

               Sample:  Calc.FanghiF.P.-106m.(4g) 0.2%NaMF
             Operator:  Roberto Angius
            Submitter:  Ing.Nicola Careddu
            File Name:  C:\WIN5100\DATA\MICRO\000-030.SMP
       Material/Liquid:  Calcare SIMIN/Water

         Test Number:  Average                 Analysis Type:  High Speed(Adj)
            Analyzed:  23/11/08 16.41.50            Run Time:  0:15 hrs:min
            Reported:  27/02/09 10.34.08       Sample Density:     2.661 g/cm³
         Liquid Visc:     0.7211 cp            Liquid Density:     0.9941 g/cm³
       Analysis Temp:    35.1 °C              Base/Full Scale:  136 /  91 KCnts/s
     Full Scale Mass:   100.0%
```



```
                                 Micromeritics

WIN5100 V2.02                   Unit 1             S/N 1             Page  4

                Sample: Calc.FanghiF.P.-106m.(4g) 0.2%NaMF
              Operator: Roberto Angius
             Submitter: Ing.Nicola Careddu
             File Name: C:\WIN5100\DATA\MICRO\000-030.SMP
        Material/Liquid: Calcare SIMIN/Water

         Test Number: Average                  Analysis Type: High Speed(Adj)
            Analyzed: 23/11/08 16.41.50             Run Time: 0:15 hrs:min
            Reported: 27/02/09 10.34.08         Sample Density:    2.661 g/cm³
         Liquid Visc:    0.7211 cp              Liquid Density:    0.9941 g/cm³
       Analysis Temp:   35.1 °C               Base/Full Scale:  136 /  91 KCnts/s
     Full Scale Mass:  100.0%
________________________________________________________________________________

                                Summary Report

      Full scale pump speed: 2                               Stir time:   30 secs
           Bubble detection: Coarse                         Stir speed: Low
              Starting Size:  150.00 µm                     Probe time:   15 secs
                Ending Size:    0.30 µm

      Parameter 1    0.000        Parameter 2    0.000        Parameter 3    0.000

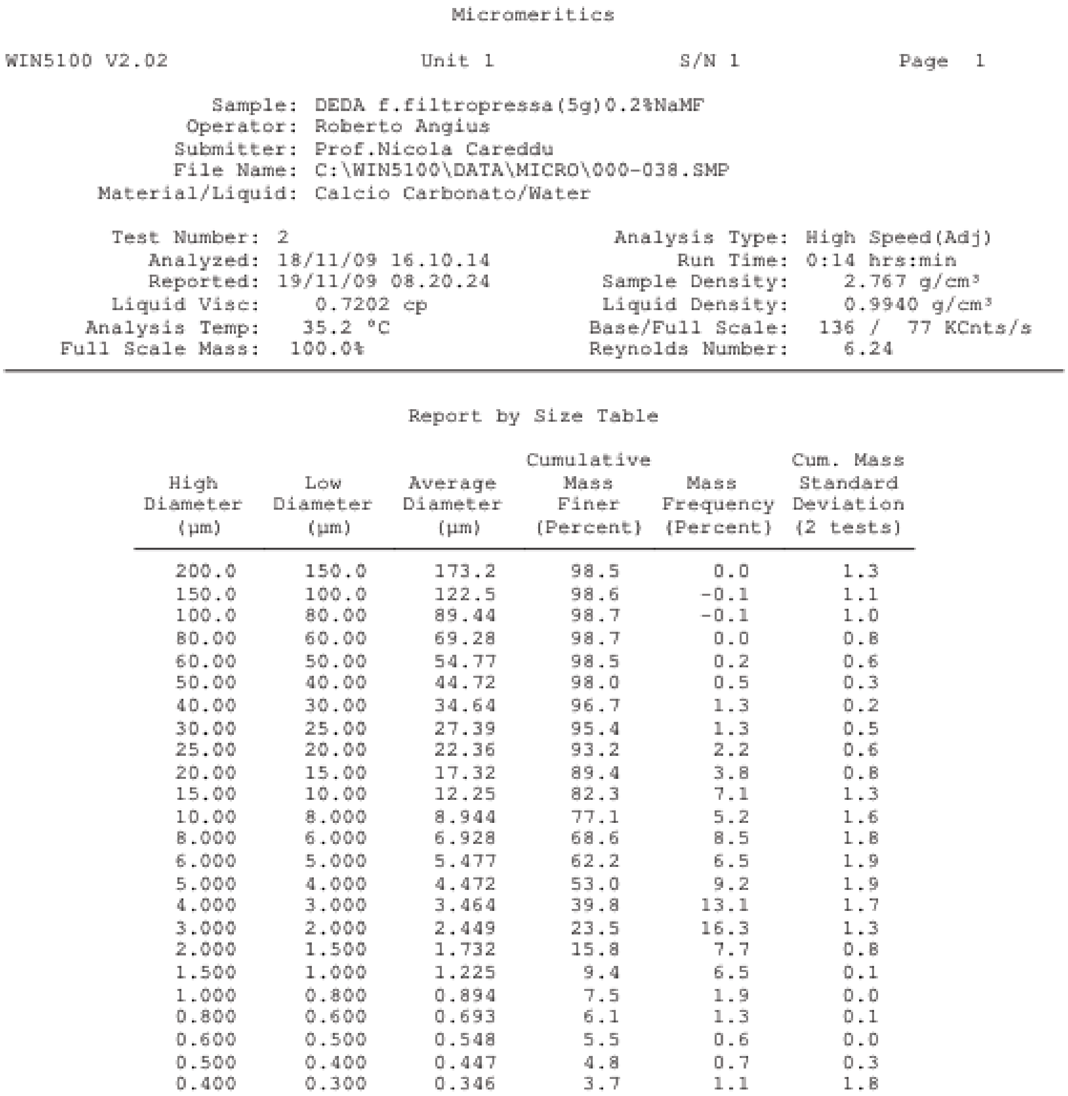
                        Mass Distribution Arithmetic Statistics
                             σ( of 2)                                    σ( of 2)
  Mode                 3.084    0.376          Median            3.638    0.106

  Peak        %                    Mean                 Standard
 Number   of Dist.*    Mean       σ of 2      Median    Deviation  Skewness  Kurtosis
________________________________________________________________________________

   1        93.1      7.394       0.430       3.873      9.469      3.120     13.151

* Peaks must comprise at least  5.00 % of the distribution.
```

1.D
DeDa



```
                                  Micromeritics

WIN5100 V2.02                    Unit 1              S/N 1            Page  1

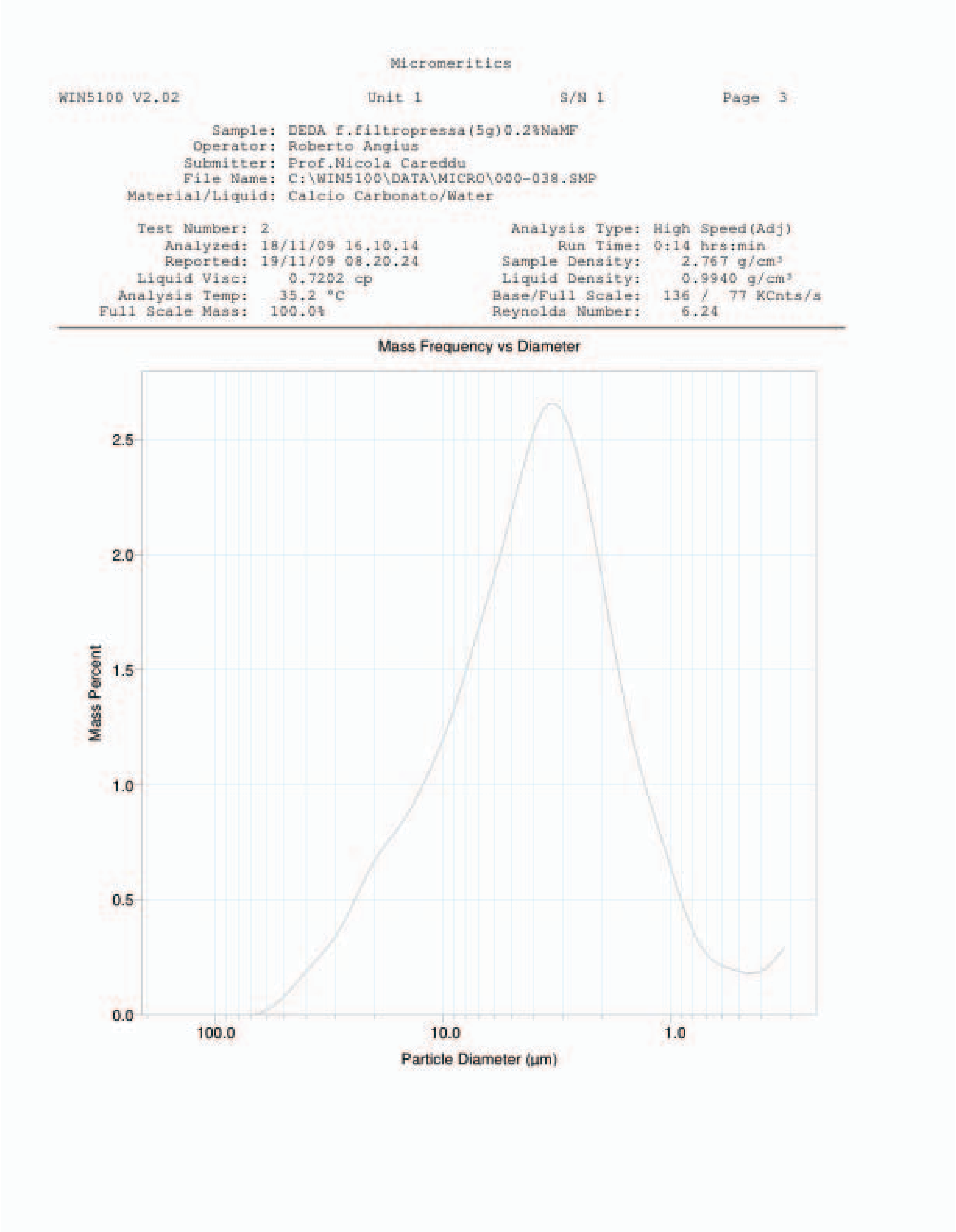
                Sample:  DEDA f.filtropressa(5g)0.2%NaMF
              Operator:  Roberto Angius
             Submitter:  Prof.Nicola Careddu
             File Name:  C:\WIN5100\DATA\MICRO\000-038.SMP
        Material/Liquid:  Calcio Carbonato/Water

         Test Number:  2                          Analysis Type:  High Speed(Adj)
            Analyzed:  18/11/09 16.10.14               Run Time:  0:14 hrs:min
            Reported:  19/11/09 08.20.24         Sample Density:     2.767 g/cm³
         Liquid Visc:     0.7202 cp              Liquid Density:     0.9940 g/cm³
       Analysis Temp:    35.2 °C               Base/Full Scale:   136 /  77 KCnts/s
     Full Scale Mass:   100.0%                 Reynolds Number:     6.24
__________________________________________________________________________________

                              Report by Size Table

                                             Cumulative            Cum. Mass
              High       Low      Average      Mass       Mass     Standard
            Diameter   Diameter   Diameter     Finer    Frequency  Deviation
              (µm)       (µm)       (µm)     (Percent)  (Percent)  (2 tests)
          ___________________________________________________________________

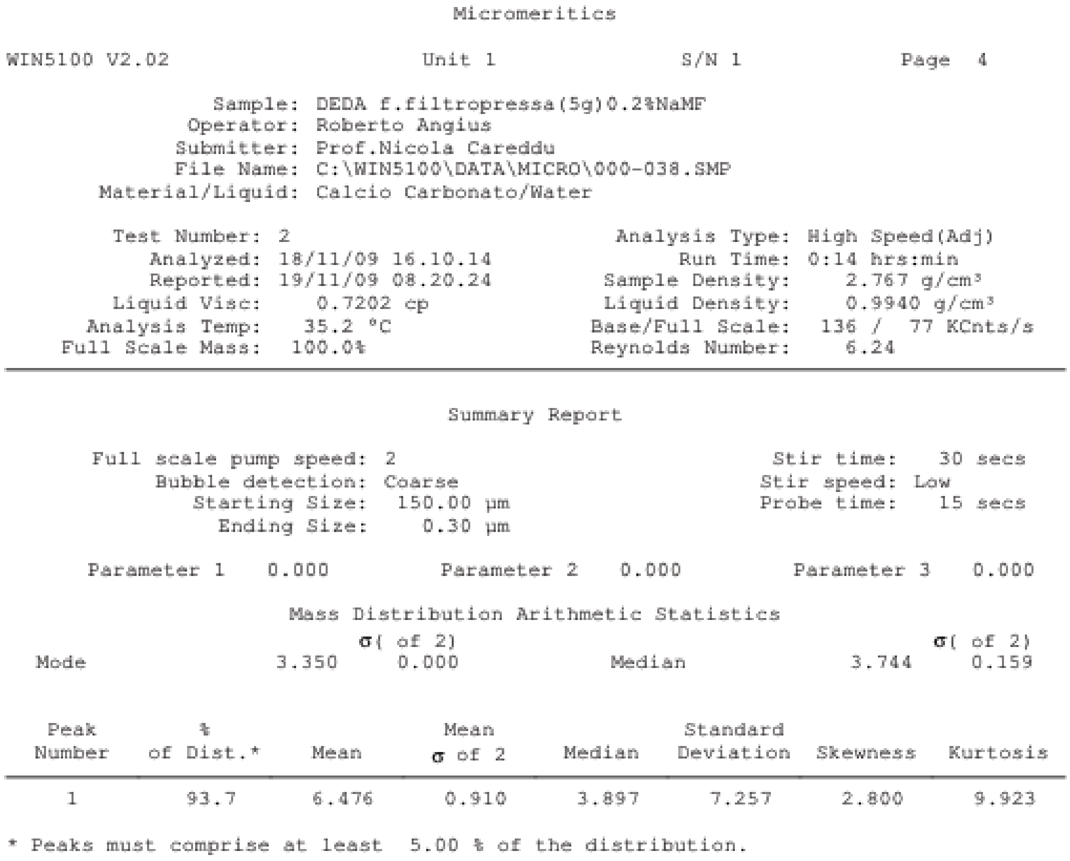
             200.0      150.0      173.2       98.5        0.0        1.3
             150.0      100.0      122.5       98.6       -0.1        1.1
             100.0      80.00      89.44       98.7       -0.1        1.0
             80.00      60.00      69.28       98.7        0.0        0.8
             60.00      50.00      54.77       98.5        0.2        0.6
             50.00      40.00      44.72       98.0        0.5        0.3
             40.00      30.00      34.64       96.7        1.3        0.2
             30.00      25.00      27.39       95.4        1.3        0.5
             25.00      20.00      22.36       93.2        2.2        0.6
             20.00      15.00      17.32       89.4        3.8        0.8
             15.00      10.00      12.25       82.3        7.1        1.3
             10.00      8.000      8.944       77.1        5.2        1.6
             8.000      6.000      6.928       68.6        8.5        1.8
             6.000      5.000      5.477       62.2        6.5        1.9
             5.000      4.000      4.472       53.0        9.2        1.9
             4.000      3.000      3.464       39.8       13.1        1.7
             3.000      2.000      2.449       23.5       16.3        1.3
             2.000      1.500      1.732       15.8        7.7        0.8
             1.500      1.000      1.225        9.4        6.5        0.1
             1.000      0.800      0.894        7.5        1.9        0.0
             0.800      0.600      0.693        6.1        1.3        0.1
             0.600      0.500      0.548        5.5        0.6        0.0
             0.500      0.400      0.447        4.8        0.7        0.3
             0.400      0.300      0.346        3.7        1.1        1.8
```



```
                                 Micromeritics
WIN5100 V2.02                      Unit 1              S/N 1           Page  3

                 Sample:  DEDA f.filtropressa(5g)0.2%NaMF
               Operator:  Roberto Angius
              Submitter:  Prof.Nicola Careddu
              File Name:  C:\WIN5100\DATA\MICRO\000-038.SMP
         Material/Liquid:  Calcio Carbonato/Water

      Test Number:  2                      Analysis Type:  High Speed(Adj)
         Analyzed:  18/11/09 16.10.14            Run Time:  0:14 hrs:min
         Reported:  19/11/09 08.20.24      Sample Density:    2.767 g/cm³
      Liquid Visc:     0.7202 cp           Liquid Density:    0.9940 g/cm³
    Analysis Temp:    35.2 °C            Base/Full Scale:  136 /   77 KCnts/s
  Full Scale Mass:   100.0%              Reynolds Number:     6.24
```



```
                              Micromeritics

WIN5100 V2.02                 Unit 1            S/N 1           Page  4

               Sample: DEDA f.filtropressa(5g)0.2%NaMF
             Operator: Roberto Angius
            Submitter: Prof.Nicola Careddu
            File Name: C:\WIN5100\DATA\MICRO\000-038.SMP
       Material/Liquid: Calcio Carbonato/Water

        Test Number: 2                        Analysis Type: High Speed(Adj)
           Analyzed: 18/11/09 16.10.14             Run Time: 0:14 hrs:min
           Reported: 19/11/09 08.20.24       Sample Density:    2.767 g/cm³
        Liquid Visc:    0.7202 cp            Liquid Density:    0.9940 g/cm³
      Analysis Temp:   35.2 °C              Base/Full Scale:  136 /  77 KCnts/s
    Full Scale Mass:  100.0%                Reynolds Number:    6.24
_____________________________________________________________________________

                              Summary Report

      Full scale pump speed: 2                            Stir time:   30 secs
           Bubble detection: Coarse                      Stir speed: Low
              Starting Size:  150.00 µm                  Probe time:   15 secs
                Ending Size:    0.30 µm

      Parameter 1   0.000        Parameter 2   0.000        Parameter 3   0.000

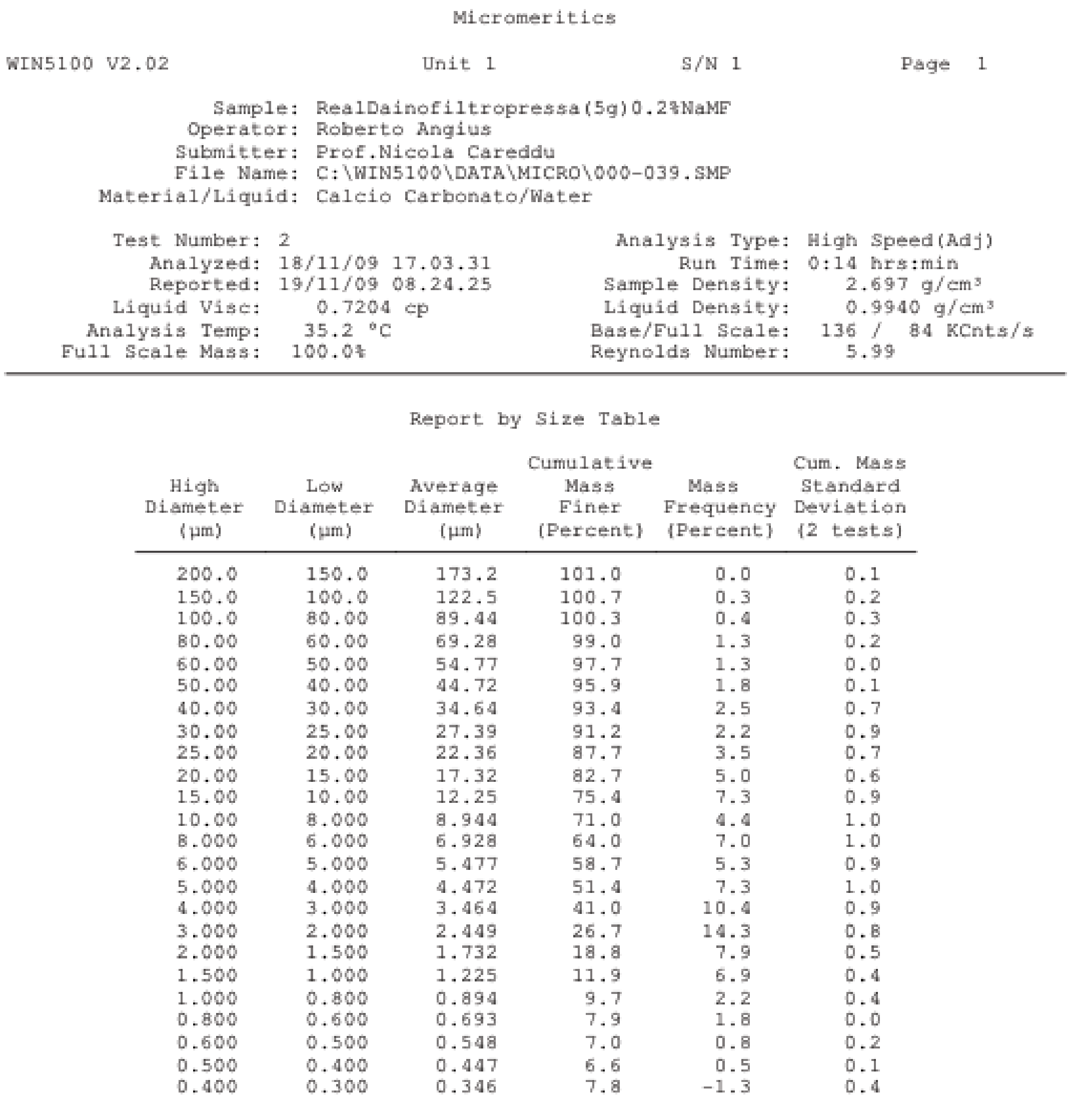
                    Mass Distribution Arithmetic Statistics
                         σ( of 2)                                     σ( of 2)
  Mode              3.350    0.000           Median             3.744    0.159

 Peak       %                  Mean              Standard
 Number  of Dist.*   Mean     σ of 2    Median   Deviation  Skewness  Kurtosis
_____________________________________________________________________________

   1        93.7     6.476     0.910     3.897     7.257     2.800     9.923

* Peaks must comprise at least  5.00 % of the distribution.
```

1.E
Daino Real



```
                               Micromeritics

WIN5100 V2.02                    Unit 1              S/N 1            Page  1

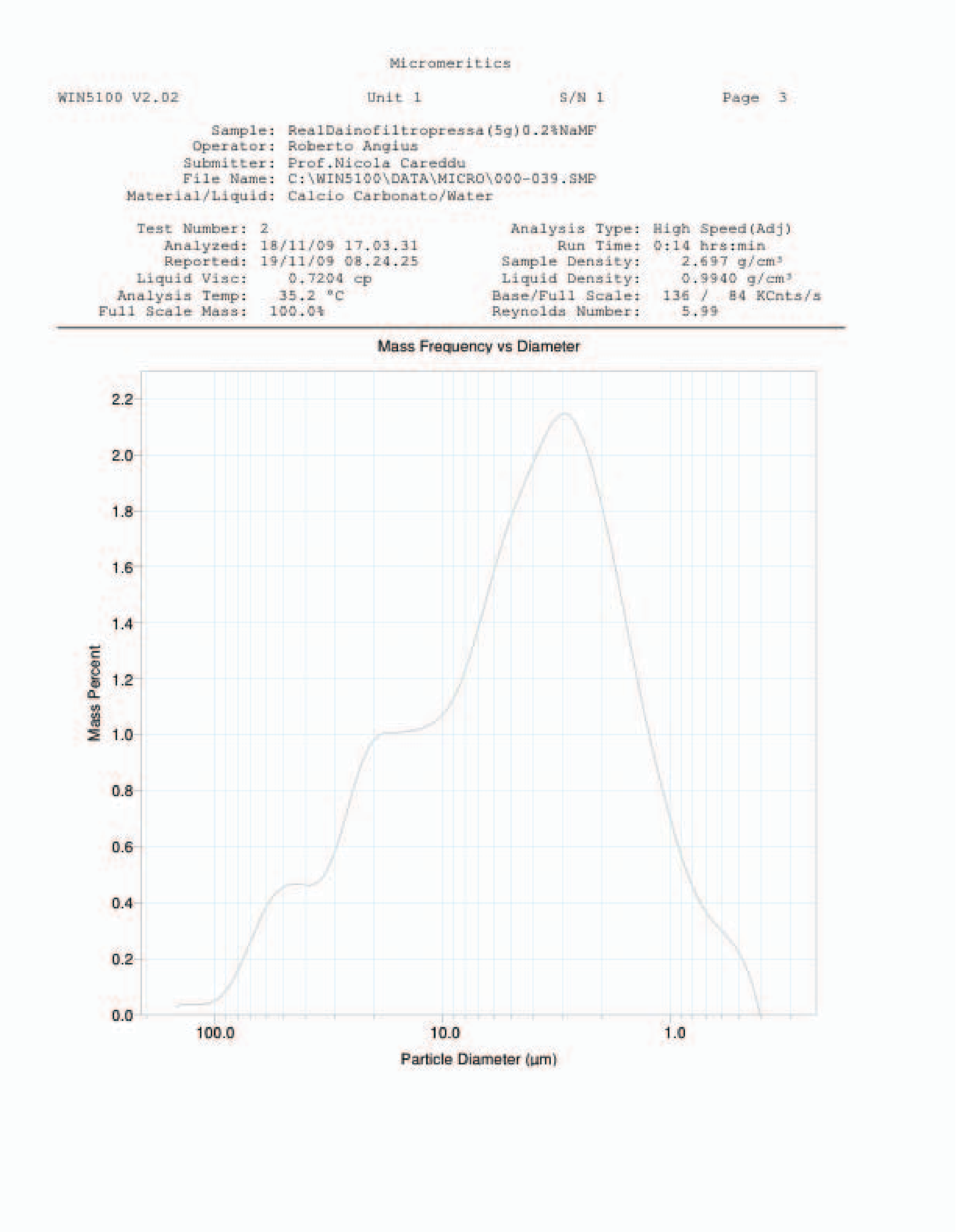
                Sample:  RealDainofiltropressa(5g)0.2%NaMF
              Operator:  Roberto Angius
             Submitter:  Prof.Nicola Careddu
             File Name:  C:\WIN5100\DATA\MICRO\000-039.SMP
       Material/Liquid:  Calcio Carbonato/Water

         Test Number:  2                      Analysis Type:  High Speed(Adj)
            Analyzed:  18/11/09 17.03.31           Run Time:  0:14 hrs:min
            Reported:  19/11/09 08.24.25     Sample Density:     2.697 g/cm³
         Liquid Visc:     0.7204 cp          Liquid Density:     0.9940 g/cm³
       Analysis Temp:    35.2 °C           Base/Full Scale:   136 /  84 KCnts/s
     Full Scale Mass:   100.0%             Reynolds Number:     5.99
_____________________________________________________________________________

                           Report by Size Table

                                    Cumulative           Cum. Mass
          High       Low     Average     Mass      Mass     Standard
        Diameter  Diameter  Diameter    Finer   Frequency  Deviation
          (µm)      (µm)      (µm)    (Percent) (Percent)  (2 tests)
        _____________________________________________________________

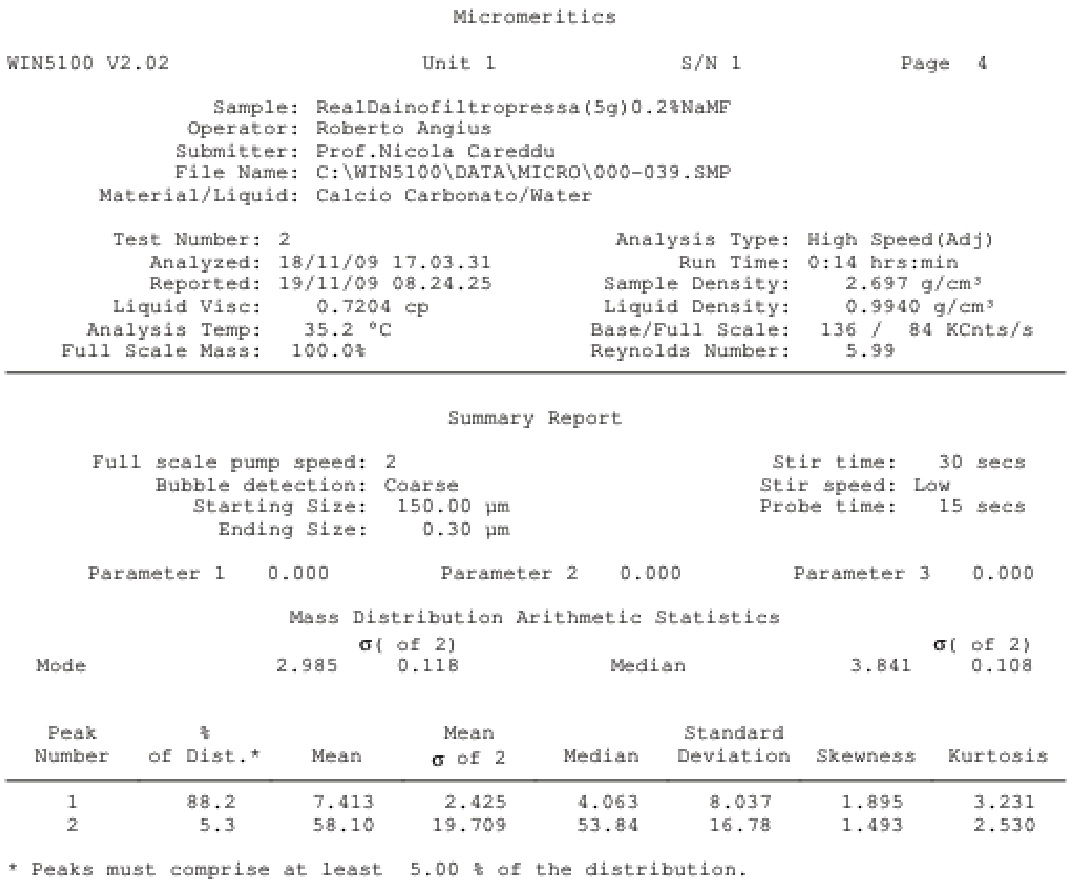
          200.0     150.0     173.2     101.0       0.0        0.1
          150.0     100.0     122.5     100.7       0.3        0.2
          100.0     80.00     89.44     100.3       0.4        0.3
          80.00     60.00     69.28      99.0       1.3        0.2
          60.00     50.00     54.77      97.7       1.3        0.0
          50.00     40.00     44.72      95.9       1.8        0.1
          40.00     30.00     34.64      93.4       2.5        0.7
          30.00     25.00     27.39      91.2       2.2        0.9
          25.00     20.00     22.36      87.7       3.5        0.7
          20.00     15.00     17.32      82.7       5.0        0.6
          15.00     10.00     12.25      75.4       7.3        0.9
          10.00     8.000     8.944      71.0       4.4        1.0
          8.000     6.000     6.928      64.0       7.0        1.0
          6.000     5.000     5.477      58.7       5.3        0.9
          5.000     4.000     4.472      51.4       7.3        1.0
          4.000     3.000     3.464      41.0      10.4        0.9
          3.000     2.000     2.449      26.7      14.3        0.8
          2.000     1.500     1.732      18.8       7.9        0.5
          1.500     1.000     1.225      11.9       6.9        0.4
          1.000     0.800     0.894       9.7       2.2        0.4
          0.800     0.600     0.693       7.9       1.8        0.0
          0.600     0.500     0.548       7.0       0.8        0.2
          0.500     0.400     0.447       6.6       0.5        0.1
          0.400     0.300     0.346       7.8      -1.3        0.4
```



```
                                  Micromeritics
WIN5100 V2.02                   Unit 1             S/N 1           Page  3

                 Sample:  RealDainofiltropressa(5g)0.2%NaMF
               Operator:  Roberto Angius
              Submitter:  Prof.Nicola Careddu
              File Name:  C:\WIN5100\DATA\MICRO\000-039.SMP
         Material/Liquid:  Calcio Carbonato/Water

       Test Number:  2                        Analysis Type:  High Speed(Adj)
          Analyzed:  18/11/09 17.03.31             Run Time:  0:14 hrs:min
          Reported:  19/11/09 08.24.25       Sample Density:     2.697 g/cm³
       Liquid Visc:     0.7204 cp            Liquid Density:     0.9940 g/cm³
     Analysis Temp:    35.2 °C              Base/Full Scale:  136 /  84 KCnts/s
   Full Scale Mass:   100.0%               Reynolds Number:     5.99
```



```
                              Micromeritics

WIN5100 V2.02                  Unit 1             S/N 1           Page  4

              Sample: RealDainofiltropressa(5g)0.2%NaMF
            Operator: Roberto Angius
           Submitter: Prof.Nicola Careddu
           File Name: C:\WIN5100\DATA\MICRO\000-039.SMP
      Material/Liquid: Calcio Carbonato/Water

        Test Number: 2                       Analysis Type: High Speed(Adj)
           Analyzed: 18/11/09 17.03.31            Run Time: 0:14 hrs:min
           Reported: 19/11/09 08.24.25       Sample Density:    2.697 g/cm³
        Liquid Visc:    0.7204 cp            Liquid Density:    0.9940 g/cm³
      Analysis Temp:   35.2 °C              Base/Full Scale:  136 /  84 KCnts/s
    Full Scale Mass:  100.0%                Reynolds Number:    5.99
_____________________________________________________________________________

                             Summary Report

      Full scale pump speed: 2                            Stir time:   30 secs
           Bubble detection: Coarse                      Stir speed: Low
              Starting Size:  150.00 µm                  Probe time:   15 secs
                Ending Size:    0.30 µm

      Parameter 1   0.000        Parameter 2   0.000        Parameter 3   0.000

                      Mass Distribution Arithmetic Statistics
                           σ( of 2)                                     σ( of 2)
  Mode                2.985     0.118          Median             3.841     0.108

  Peak        %                   Mean                   Standard
  Number   of Dist.*    Mean      σ of 2      Median     Deviation  Skewness  Kurtosis
_____________________________________________________________________________________

    1        88.2      7.413      2.425       4.063       8.037      1.895      3.231
    2         5.3      58.10     19.709       53.84       16.78      1.493      2.530

* Peaks must comprise at least  5.00 % of the distribution.
```

APPENDIX 2

2.A

Quality control Actlab Laboratory for ICP-Analysis – Part I

(Chapter 5.3.4)

Analyte Symbol	Unit Symbol	Detection Limit	WMG-1Meas	WMG-1Cert	NIST 694 Meas	NIST 694 Cert	DNC-1Meas	DNC-1Cert	GBW07113Meas	GBW07113Cert	GXR-2Meas	GXR-2Cert	NIST 163	NIST 1633b Cert	SY-4Meas	SY-4Cert
SiO2	%	0.01			10,94	11,2	47,23	47	69,63	72,8			48,53	49,2	50,33	49,9
Al2O3	%	0.01			1,87	1,8	18,25	18,3	12,43	13			28,62	28,4	20,53	20,69
Fe2O3(T)	%	0.01			0,74	0,79	9,7	9,93	3,08	3,21			11,29	11,1	6,15	6,21
MnO	%	0.001			0,013	0,0116	0,148	0,149	0,139	0,14			0,019	0,02	0,109	0,108
MgO	%	0.01			0,34	0,33	10,22	10,1	0,14	0,16			0,76	0,8	0,5	0,54
CaO	%	0.01			42,51	43,6	11,56	11,3	0,59	0,59			2,2	2,11	8,26	8,05
Na2O	%	0.01			0,88	0,86	1,93	1,87	2,44	2,57			0,27	0,27	7,05	7,1
K2O	%	0.01			0,55	0,51	0,23	0,234	5,35	5,43			2,34	2,35	1,71	1,66
TiO2	%	0.001			0,114	0,11	0,471	0,48	0,269	0,3			1,3	1,32	0,291	0,287
P2O5	%	0.01			30,17	30,2	0,09	0,09	0,05	0,05			0,55	0,53	0,13	0,131
Sc	ppm	1					31	31	5	5			41	41	1	1,1
Be	ppm	1					< 1	1	4	4					3	2,6
V	ppm	5			1660	1740	158	148	<5	5			311	296	5	8
Cr	ppm	20	690	770			270	285			30	36				
Co	ppm	1	191	200			59	54,7			9	8,6				
Ni	ppm	20	2510	2700			260	247			< 20	21				
Cu	ppm	10	6050	5900			110	96			80	76				
Zn	ppm	30	110	110			70	66			560	530				
Ga	ppm	1	10	10,3			14	15			35	37				
Ge	ppm	1					2	1,3								
As	ppm	5	9	7			<5	0,2			24	25				
Rb	ppm	2					4	4,5			77	78				
Sr	ppm	2					144	145	41	43			1044	1040	1187	1191
Y	ppm	2					17	18	44	43					119	119
Zr	ppm	4					35	41	372	403					519	517
Nb	ppm	1	6	6			2	3			10	11				
Mo	ppm	2	< 2	1,4			< 2	0,7			< 2	2,1				
Ag	ppm	0.5	2,3	2,7			< 0.5	0,027			16,5	17				
In	ppm	0.2									< 0.2	0,252				
Sn	ppm	1	3	2,2							2	1,7				
Sb	ppm	0.5	3,2	1,8			1,4	0,96			48,2	49				
Cs	ppm	0.5	< 0.5	0,48			< 0.5	0,34			5,3	5,2				
Ba	ppm	3					108	114	485	506			719	709	358	340
La	ppm	0.1	8,5	8,2			4,6	3,8			28,3	25,6				
Ce	ppm	0.1	17,7	16			9,7	10,6			54,3	51,4				
Pr	ppm	0.05					1,24	1,3								
Nd	ppm	0.1	9,4	9			5,5	4,9			20,2	19				
Sm	ppm	0.1	2,3	2,3			1,5	1,38			3,7	3,5				
Eu	ppm	0.05	0,69	0,82			0,59	0,59			0,68	0,81				
Gd	ppm	0.1					2	2			3,2	3,3				
Tb	ppm	0.1	0,4	0,3			0,4	0,41			0,5	0,48				
Dy	ppm	0.1	2,3	2,8			2,8	2,7			2,8	3,3				
Ho	ppm	0.1	0,5	0,5			0,6	0,62								
Er	ppm	0.1					1,9	2								
Tm	ppm	0.05	0,19	0,2			0,31	0,38			0,27	0,3				
Yb	ppm	0.1	1,2	1,3			2	2,01			1,7	2,04				
Lu	ppm	0.04	0,18	0,21			0,29	0,32			0,25	0,27				
Hf	ppm	0.2	1,5	1,3			1,1	1,01			6,1	8,3				
Ta	ppm	0.1	0,3	0,5			< 0.1	0,098			0,7	0,9				
W	ppm	1	< 1	1,3			< 1	0,2			2	1,9				
Tl	ppm	0.1					< 0.1	0,026			0,7	1,03				
Pb	ppm	5	17	15			7	6,3			666	690				
Bi	ppm	0.4					< 0.4	0,02			< 0.4	0,69				
Th	ppm	0.1	1,2	1,1			0,3	0,2			8,3	8,8				
U	ppm	0.1	0,8	0,65			< 0.1	0,1			3	2,9				

2.B
Quality control Actlab Laboratory for ICP-Analysis – Part II

(Chapter 5.3.4)

Analyte Symbol	Unit Symbol	Detection Limit	CTA-AC-1Me	CTA-AC-1C	BIR-1a Meas	BIR-1a Cert	NCSDC8631	NCSDC863	NCSDC70014Me	NCSDC70014C	NCSDC7000	NCSDC700	OREAS 1	OREAS 100a (Fu	OREAS 101a	OREAS 10	JR-1Meas	JR-1Cert
SiO2	%	0.01																
Al2O3	%	0.01																
Fe2O3(T)	%	0.01																
MnO	%	0.001																
MgO	%	0.01																
CaO	%	0.01																
Na2O	%	0.01																
K2O	%	0.01																
TiO2	%	0.001																
P2O5	%	0.01																
Sc	ppm	1																
Be	ppm	1																
V	ppm	5																
Cr	ppm	20			370	382					30	30					<20	2,83
Co	ppm	1	<1	2,72	54	51,4			25	26,2	3	3,7	16	18,1	46	48,8	<1	0,83
Ni	ppm	20			160	166			70	70,9	<20	2,8					<20	1,67
Cu	ppm	10	60	54	130	126			2670	2600	780	960	170	169	430	434	<10	2,68
Zn	ppm	30	30	38	80	71			7400	7400	100	100					<30	30,6
Ga	ppm	1			15	16			25	25,2	16	16,5					16	16,1
Ge	ppm	1			2	1,5					11	11,2					3	1,88
As	ppm	5			<5	0,44			> 2000	7900	70	69,9					17	16,3
Rb	ppm	2			<2	0,25					505	500					247	257
Sr	ppm	2																
Y	ppm	2																
Zr	ppm	4																
Nb	ppm	1			<1	0,6			12	46,9							17	15,2
Mo	ppm	2			<2	0,5			> 100	270	> 100	980	23	24,1	21	21,9	3	3,25
Ag	ppm	0.5			<0.5	0,036			17,3	16,7	1,5	1,8					<0.5	0,031
In	ppm	0.2									1,3	1,3					<0.2	0,028
Sn	ppm	1			<1	0,65			> 1000	44700	> 1000	1700					3	2,86
Sb	ppm	0.5			0,9	0,58			180	180	4,2	3,1					1,6	1,19
Cs	ppm	0.5			<0.5	0,005					45	41					20,7	20,8
Ba	ppm	3																
La	ppm	0.1	> 2000	2176	1,3	0,62			47,2	45,3	26,5	23,7	273	260	839	816	22,5	19,7
Ce	ppm	0.1	> 3000	3326	3,1	1,95			87,4	87	63,4	60,3	476	463	1400	1396	50,6	47,2
Pr	ppm	0.05			0,49	0,38			10	10,8	8,12	7,9	47,6	47,1	130	134	6,1	5,58
Nd	ppm	0.1	1110	1087	2,8	2,5			37,9	39,9	32,6	32,9	151	152	392	403	23,9	23,3
Sm	ppm	0.1	162	162	1,2	1,1			7,8	8	12,8	12,5	23,6	23,6	49,5	48,8	5,9	6,03
Eu	ppm	0.05	44,6	46,7	0,53	0,54			1,62	1,8	0,11	0,16	3,56	3,71	7,91	8,06	0,28	0,3
Gd	ppm	0.1	131	124	1,9	1,85			7	7,4	15,3	14,8	21	23,6	37,2	43,4	5,6	5,06
Tb	ppm	0.1	14,5	13,9	0,4	0,36			1,1	1,1	3,5	3,3	3,7	3,8	5,4	5,92	1	1,01
Dy	ppm	0.1			2,5	2,5			6,2	6,7	21,4	20,7	22,4	23,2	30,8	33,3	6,1	5,69
Ho	ppm	0.1			0,6	0,57			1,2	1,3	4,5	4,5	4,8	4,81	6,4	6,46	1,3	1,11
Er	ppm	0.1			1,6	1,7			3,3	3,5	13,1	13,4	14	14,9	18,7	19,5	3,9	3,61
Tm	ppm	0.05			0,27	0,26			0,52	0,57	2,42	2,2	2,32	2,31	2,88	2,9	0,69	0,67
Yb	ppm	0.1	10,7	11,4	1,7	1,65			3,3	3,3	16,5	14,9	14,9	14,9	17,9	17,5	4,6	4,55
Lu	ppm	0.04	1,07	1,08	0,24	0,26			0,47	0,5	2,35	2,4	2,11	2,26	2,46	2,66	0,67	0,71
Hf	ppm	0.2	1,9	1,13	0,7	0,6											5	4,51
Ta	ppm	0.1	2,6	2,65	<0.1	0,04			3,8	16,2							1,7	1,86
W	ppm	1			<1	0,07			347	680	2300	2200					3	1,59
Tl	ppm	0.1			<0.1	0,01					2,1	1,8					1,2	1,56
Pb	ppm	5			<5	3			> 10000	27200	65	81,2			72	19	20	19,3
Bi	ppm	0.4			<0.4	0,02			80,3	80,3	121	680					0,5	0,56
Th	ppm	0.1	22,8	21,8	0,2	0,03	26,1	23,6			28,7	28,3	51,3	51,6	35,4	36,6	25,9	26,7
U	ppm	0.1	4,3	4,4	<0.1	0,01							141	135	420	422	9,3	8,88

2.C

The ICP-AES data for the SIMG1 and SIMG2 fractions (Chapter 5.3.4)

Descrizione	Fe_2O_3 %	SiO_2 %	Al_2O_3 %	Na_2O %	K_2O %	Ca %	MgO %	MnO %	TiO_2 %
C 01	0.0754		0.0136	0.1334	0.0128	36.45	0.4272	0.0034	<0.0010
C 02	0.0246		0.0116	0.374	0.028	37.07	0.6424	0.0038	<0.0038
C 03	0.0252		0.0106	0.0342	0.006	38.50	0.383	0.0038	<0.0010
C 04	0.0258		0.0346	0.1246	0.013	36.53	0.3876	0.0036	<0.010
C 05	0.0286		0.0056	0.116	0.0098	34.44	0.4128	0.0036	<0.0010
C 06	0.0318		0.0168	0.2756	0.0184	35.71	0.5106	0.0004	<0.0010
C 07	0.0054		0.0106	0.108	0.0058	34.98	0.4086	0.0036	<0.0010
C 08	0.0650		0.0342	0.0756	0.0154	36.27	0.4780	0.0062	<0.0010
C 09	0.0480		0.0356	0.1176	0.0156	33.67	0.4756	0.0052	<0.0010
C 10	0.0564		0.0408	0.0340	0.0086	33.54	0.436	0.0056	<0.0010
C 11	0.0446		0.0308	0.0180	0.0044	34.62	0.3992	0.0050	<0.0010
C12	0.0348		0.0264	0.0764	0.0136	34.72	0.4296	0.0052	<0.0010
C 13	0.0780		0.0604	0.1582	0.0216	35.15	0.5334	0.0064	<0.0010
C 14	0.1955		0.0746	0.1026	0.0136	35.27	0.5046	0.0066	<0.0010

Legend

$SIMG_1$ +75µm	C1
$SIMG_1$ -75+53 µm	C2
$SIMG_1$ -53+38 µm	C3
$SIMG_1$ -38+20 µm	C4
$SIMG_1$ -20+10 µm	C5
$SIMG_1$ -10+5 µm	C6
$SIMG_1$ -5 µm	C7
$SIMG_2$ +75	C8
$SIMG_2$ -75+53 µm	C9
$SIMG_2$ -53+38 µm	C10
$SIMG_2$ -38+20 µm	C11
$SIMG_2$ -20+10 µm	C12
$SIMG_2$ -10+5 µm	C13
$SIMG_2$ -5 µm	C14

APPENDIX 3

3.A

ICP-Analysis – Tenax Frankfurt 800

Abrasive - 1 **Tenax Frankfurt 800**	**[ppm]**
Al	0.36
Ca	27.85
Fe	13.01
Mg	9.71
Si	19.15
Be	1.223
Ti	180.824
V	95.423
Cr	39.703
Mn	70.236
Co	140.858
Ni	63.998
Cu	132.374
Ge	0.355
Rb	27.277
Zr	6.706
Nb	2.98
Mo	4.236
Sn	6.836
Sb	13591.25
Te	1.453
Cs	2.509
Rh	ND
Hf	0.268
Ta	0.196
W	2.137
Tl	2.077
Pb	139.431
Th	3.446
U	1.608
Re	ND

ICP-Analysis – Tenax Frankfurt 500

Abrasive – 2 Tenax Frankfurt 500	**[ppm]**
Al	0.30575
Ca	45.206
Fe	23.85575
Mg	9.92575
Si	17.559
Be	140.858
Ti	63.998
V	132.374
Cr	0.355
Mn	27.277
Co	6.706
Ni	2.98
Cu	4.236
Ge	6.836
Rb	13591.25
Zr	1.453
Nb	2.509
Mo	ND
Sn	0.268
Sb	0.196
Te	2.137
Cs	2.077
Rh	139.431
Hf	3.446
Ta	1.608
W	ND
Tl	1.223
Pb	180.824
Th	95.423
U	39.703
Re	70.236

ICP-Analysis – Tenax Frankfurt 360

Abrasive – 3 Tenax Frankfurt 360	[ppm]
Al	0.44875
Ca	39.65325
Fe	3.43075
Mg	9.3225
Si	19.38375
Be	1.795
Ti	158.613
V	13.723
Cr	37.29
Mn	77.535
Co	566.784
Ni	160.221
Cu	51.68
Ge	0.359
Rb	31.781
Zr	6.585
Nb	3.324
Mo	2.723
Sn	0.189
Sb	39.203
Te	1.009
Cs	4.181
Rh	ND
Hf	0.234
Ta	0.224
W	1.993
Tl	1.376
Pb	94.15
Th	2.869
U	1.739
Re	ND

ICP-Analysis – Tenax Frankfurt 220

Abrasive – 4 Tenax Frankfurt 220	**[ppm]**
Al	0.33375
Ca	40.46325
Fe	7.81975
Mg	28.411
Si	27.7865
Be	1.335
Ti	161.853
V	31.279
Cr	113.644
Mn	111.146
Co	4.927
Ni	246.68
Cu	51.062
Ge	0.42
Rb	10.124
Zr	5.679
Nb	1.234
Mo	2.021
Sn	6.054
Sb	78.935
Te	0.794
Cs	1.896
Rh	ND
Hf	0.225
Ta	0.401
W	2.806
Tl	0.98
Pb	102.182
Th	1.149
U	0.72
Re	ND

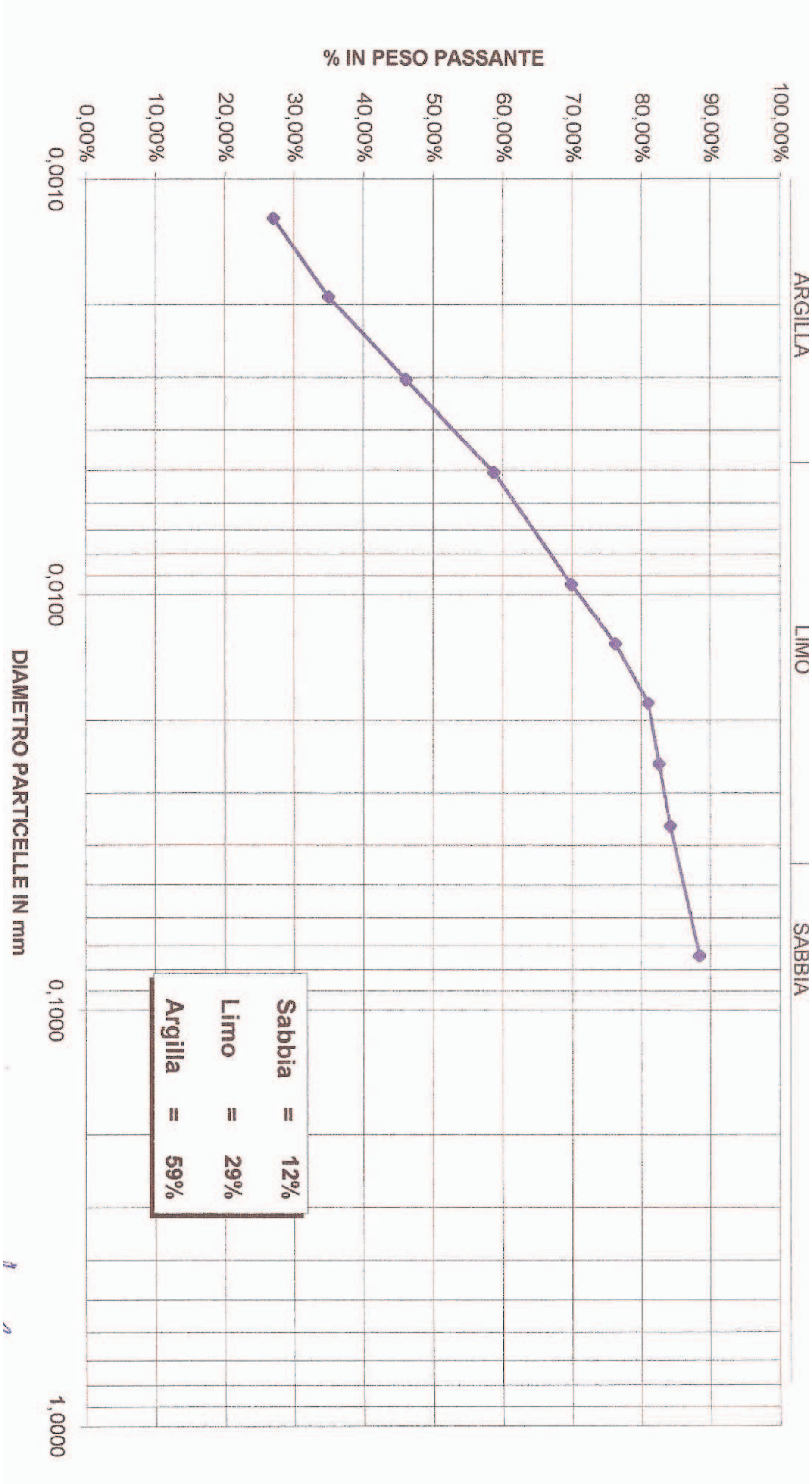
ICP-Analysis – Frankfurt chemical attack

Abrasive – 4 **Tenax Frankfurt chemical attack**	**[ppm]**
Al	0.1035
Ca	28.748
Fe	1.59475
Mg	5.309
Si	1.75675
Be	0.414
Ti	114.992
V	6.379
Cr	21.236
Mn	7.027
Co	1.556
Ni	23.13
Cu	42.848
Ge	0.164
Rb	5.751
Zr	-2.388
Nb	0.054
Mo	1.267
Sn	1.116
Sb	27.721
Te	0.665
Cs	1.127
Rh	ND
Hf	0.012
Ta	0.041
W	1.045
Tl	0.714
Pb	110.867
Th	0.028
U	0.173
Re	ND

APPENDIX 4

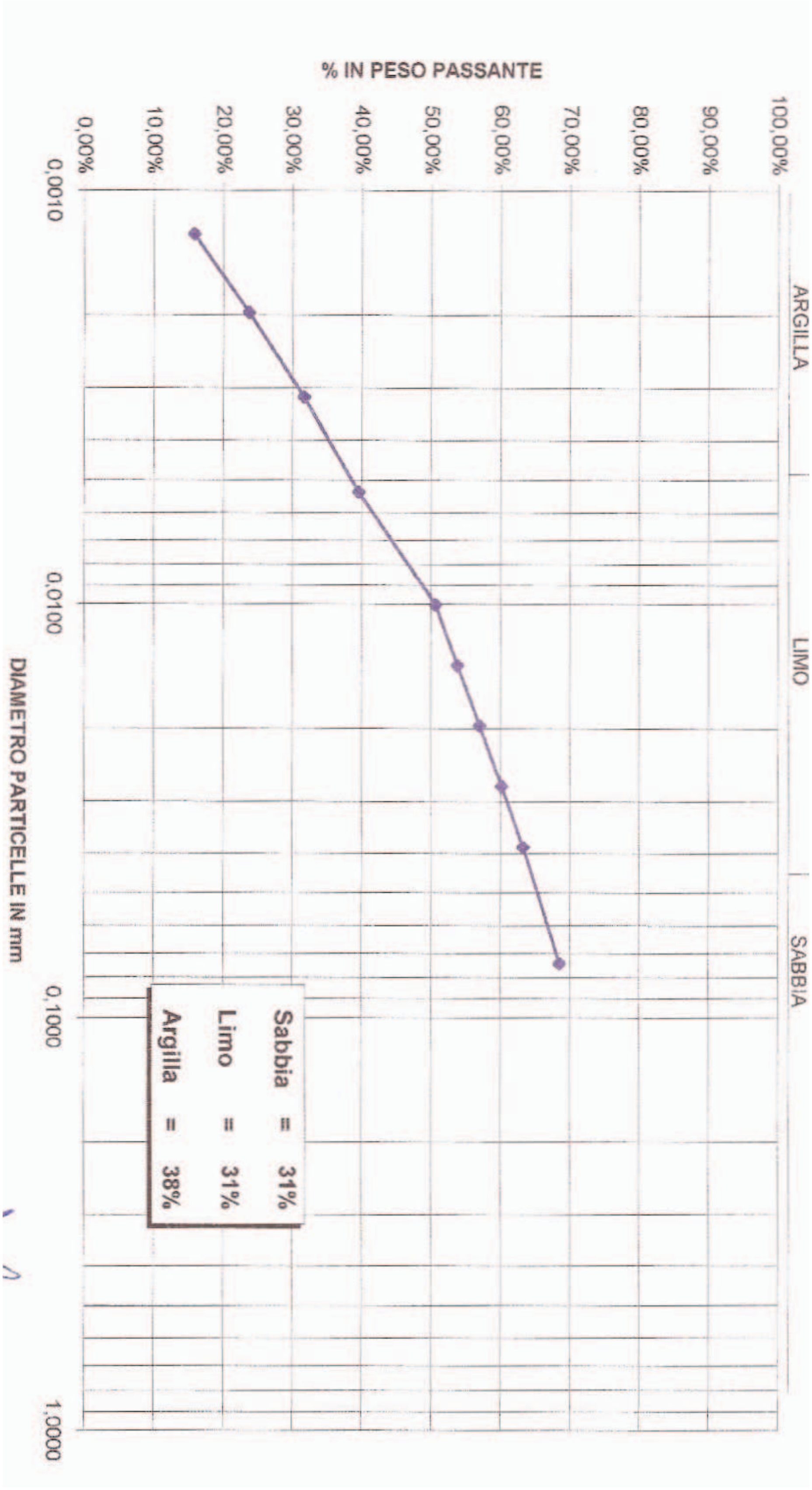
4.A

Grain size distribution YCM - (Chapter 7.2.1.1)



4.B

Grain size distribution BCU - (Chapter 7.2.1.2)



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