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## Sustainable management of natural stone waste. A proposed re-use for the production of mortars and the assessment of their potential $CO_2$ sequestration capacity

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**Sustainable management of natural stone waste. A proposed re-use for the production of mortars and the assessment of their potential $CO_2$ sequestration capacity.**

# Abstract

Quarrying activity usually generates significant amounts of waste. Generally, the processed quarrying production accounts for 30% of total stone extracted, whilst waste (quarrying waste and processing waste) amounts to about 70% of total stone extracted.

Not only could coping with waste be environmentally damaging, but it is also economically expensive for the stone industry, which in addition has to deal with the economic loss caused by the lower efficiency of quarrying. Some re-uses of natural stone waste, such as the production of aggregates, have already been investigated, but they are not profitable for most quarrying companies. Other re-uses of stone waste are related to economic fields which are too distant from quarrying companies to foster their commitment on their re-use (such as agriculture; paper industry; etc.). In fact, they are encouraged to sell waste at increasingly lower prices so as to get rid of it, reducing landfill costs. This research identifies the re-use of stone waste in the construction industry as the most profitable use, since quarrying activity is strictly related to the building industry. Hence, quarrying companies have the necessary skills and expertise to evaluate the economic risks, thus they are more eager to undertake the production of new by-products.

Therefore, the generic goal of this work is to convert natural stone waste into some by-products with a renewed environmental and economic value. To this purpose, the production of cement-based and lime-based materials such as mortars (mixtures of a binder, fine aggregates and water) was identified amongst the possible re-uses as the most suitable one, since stone waste can be re-used to some extent as a substitute of the binder (cement or lime) fraction and for the production of the aggregate fraction, thus achieving a higher re-use rate. In fact, since mortars have no structural use, their requirements are far more flexible than materials such as concrete and it is possible to re-use higher percentages of waste in their manufacture.

A further goal of this dissertation was to enhance the environmental advantages of re-using stone waste for the production of mortars by investigating their $CO_2$ sequestration capacity, since a percentage of $CO_2$ emissions from the production of mortars is reabsorbed as the mortar hardens, owing to carbonation. Indeed, Portland cement production is responsible for 7% of annual $CO_2$ emissions, due to the calcination reaction. Nonetheless, a secondary effect of carbonation is the uptake of atmospheric $CO_2$, which reacts with calcium hydroxide in mortars and precipitates as calcium carbonate. Although $CO_2$ uptake figures are far from the performance of other materials (such as coal ash and industrial residues), it should be pointed out that mortars have great potential, since their use in all built-up environments is impressively widespread.

Initially, the assessment of the $CO_2$ uptake of some selected commercial mortars by means of accelerated carbonation tests was undertaken through an experimental procedure, in order that a standard methodology and a set of operative parameters could be established. Then, some mortar mixtures constituted by stone waste were manufactured and henceforth called “ecological mortars”. These mixtures underwent the same carbonation tests as the commercial mortars, so as to permit a comparison between their performance.

The obtained experimental results showed that both the commercial and the ecological mortars are capable to take up $CO_2$. In particular, despite showing fairly lower figures, the “ecological mortars” reported a carbon absorption during the first 28 days of curing exceeding 6% of that emitted in the calcination reaction occurring during the production process.

Low though they may seem, this value could represent a significant amount considering the period of service life, and after the service life (i.e. after demolition) of mortars.

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# Introduction

*Source of the Problem*

The need for environmental safeguards has grown more and more over the past decades. Human activity may bring about harmful effects on the world as we know it, and we should deal with issues such as environmental sustainability, preservation of natural resources, energy efficiency, climate change, environmental impact assessment, and so on.

Industrialized Countries have undertaken environmental safeguard policies since the Kyoto Protocol (1997), either by trying to contain greenhouse gas (GHG) emissions or by minimizing the exploitation of non renewable resources. Cities are targeted by these policies as they are resource-consuming entities on account of their high population density. In 2008, about half of the world's population was concentrated in cities, and projections show that by 2030 this percentage will grow by up to 60%. Moreover, cities are also responsible for more than 70% of global $CO_2$ emissions (OECD/IEA, 2008).

In this context, building activity is the major cause of demand for construction materials. Indeed, the need for mineral raw materials makes quarrying activity strategically important in the global economy. Construction materials, either aggregates (i.e. sand, gravel and crushed stone) or dimension stones, are used in the development of all built-up environments, such as housing, civil engineering works (e.g. local hospitals, schools, bridges and flood protection, structures, etc.), roads and other infrastructures (e.g. railways), and so on (UEPG, 2009). Consequently, while quarrying activity is essential for the development of society, it could lead to the impoverishment of the environment because of excessive extraction of non renewable resources.

Additionally, quarrying activity usually generates significant amounts of natural stone waste. Usually, after the extraction and the industrial production process, stone waste is either used for the creation of squares within the quarry, in which quarry products are temporarily stocked or trucks are parked, or stored in dumps. Usually, this waste accounts for 50% of total stone extracted (Sardegna Ricerche, 2002). For marble and granite production, up to 70% of the materials are wasted in the industrial processes. 40% of marble waste is formed by small fragments with low or zero economic value. For this reason, they are often dumped in landfills (Aukour and Al-Qinna, 2008). Actually, some quarries by their very nature tend not to produce large amounts of waste: this is the case of the quarries of aggregates. Some other quarries, especially those that produce dimension stone, usually bring out notable amounts of waste. The reason behind this is that dimension stones are natural rock materials, such as granite, marble, limestone, sandstone, and slate, quarried for commercial purposes. Extracted materials are formed into blocks, slabs, tiles, etc, which are required to meet particular specifications, e.g. size and shape, to be economically attractive and sold worldwide. As a consequence, large amounts of materials are left out in this type of quarry, which raises the issue of their adequate disposal of stone waste.

Nonetheless Since these materials have the same chemical composition as the original dimension stone, instead of their costly and potentially environment-damaging dumping, they could be converted into products with a renewed economic value. For instance, marble originates calcium carbonate as waste, while granite gives rise to silica aluminates. There is a constant demand for these two types of mineral, not only from the construction industry, but also from the chemical, automotive, aerospace, food, pharmaceutical and other industries.

In addition, several industrialized countries have recently encouraged the recycling of a particular inert waste stream, construction and demolition waste (CDW). The aggregates obtained from the recycling process can be used without a difficult manufacturing process in road filling, railway ballast or armor stones. Also, their use in the production of high quality materials such as ready-mixed concrete, precast products, asphalts, etc. has been investigated by several studies. Evidently, the available literature mainly focuses on the recycling of CDW, and little research has been developed on the search for an efficient method for converting natural stone waste into an economically valuable resource, even though this kind of waste generally does not present as many impurities as CDW. In fact, because of the various origins of CDW, the differing local building techniques, the local availability of raw and building materials, etc., their composition is heterogeneous and rather changeable, e.g. masonry, concrete waste, natural earth, light fractions formed by paper, plastic, wood, and ferrous materials.

Conversely, the re-use of natural stone waste from quarrying activity is generally characterized by a modest presence or a total absence of pollutants. According to the European Waste Catalogue included in the EU Directive 2000/532/EC, natural stone waste is classified as harmless “waste from stone cutting and sawing other than those mentioned under item 010407”.

To sum up, while quarrying activity is essential for the development of society, it could lead to the impoverishment of the environment because of excessive extraction of non-renewable resources. For this reason, this work aims to propose the replacement of natural materials with re-used materials for the construction sector. Additionally, in order to evaluate the economic feasibility of the suggested process, along with the environmental risks and opportunities, a market analysis and the scenario of the global dimension stone sector will be provided in the first chapter of the thesis.

### *Objectives and significance of the study*

The primary goal of this work is to convert natural stone waste into some by-products with a renewed environmental and economic value instead of its costly and potentially environment-damaging dumping. The possibilities of re-using stone waste were analysed, so as to identify some by-products whose production may result economically advantageous for the stone industry which, consequently, would avoid the storage in dumps.

Concerning stone waste re-use, there is a number of studies focused on finer portions, at the micrometre scale (Corinaldesi et al., 2010; Marras, 2010). In addition, this research took into consideration and physically and chemically characterized a wider range of waste typologies from quarrying activity. Furthermore, current re-uses of stone waste are related to economic fields which are too distant from quarrying enterprises to foster their commitment on their re-use (such as agriculture; paper industry; etc.). They are encouraged to sell waste at increasingly lower prices so as to get rid of it, with the only advantage of reducing landfill costs. The re-use of stone waste in the construction industry is identified as the most profitable use in this work, since quarrying activity is strictly related to the building industry. Hence, quarrying companies have the necessary skills and expertise to evaluate the economic risks, thus they are more eager to undertake the production of new by-products.

Several previous studies concentrated on re-using little amounts of waste. A case in point could be the re-use of waste as aggregates in the production of structural concrete, with a substitution percentage below 10-15% in the mix-design (Corinaldesi et al., 2010). This research has considered cement- and lime-based materials (mortars) as appropriate by-products. In fact, since mortars have no structural use, their requirements are far more flexible and it is possible to re-use higher percentages of waste. Therefore, some different experimental mix-designs were produced and considered as “ecological mortars” since their use could minimize damage to the environment and reduce the exploitation of natural resources.

Besides, another important goal of this study is to enhance the environmental advantages of re-using stone waste for the production of mortars by investigating their $CO_2$ uptake capacity, since a percentage of $CO_2$ emissions from the production of mortars is reabsorbed as the it hardens, owing to carbonation.

### *Carbon Dioxide Emissions*

Carbon dioxide is one of the major GHG gases (along with nitrogen oxide and methane) which absorbs part of the sun's radiation that continually strikes the Earth, warming it. Whilst the presence of greenhouse gases in the atmosphere is a natural phenomenon, provided by vegetation, volcanism, and natural rock weathering, also anthropogenic activities can produce it, principally by burning fossil fuels and biomass, and as an industrial by-product (e.g., cement production). As a result, atmospheric carbon concentration has multiplied, amounting to 391 ppm and exceeding the pre-industrial levels by about 40%, as displayed in Figure 1.

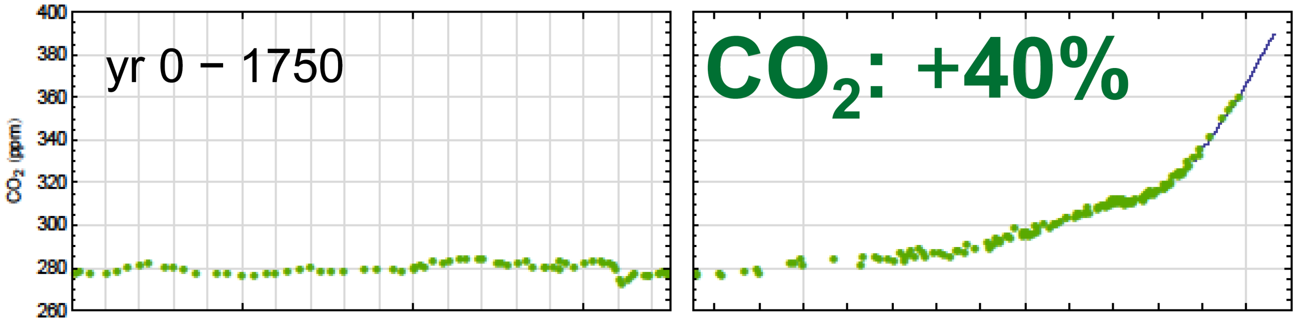

**Figure 1**. Increase in carbon dioxide concentrations from 1750 (Stocker and Dahe, 2013).

The sector of energy, through the combustion of fossil fuels such as coal, oil, and gas, provokes approximately two-thirds of global greenhouse-gas emissions of the total output (OECD/IEA, 2013). In fact, despite several policies undertaken by world governments aimed at improving energy efficiency and fostering non-fossil renewable sources (e.g. the President’s Climate Action Plan in the United States, the Chinese plan to limit the share of coal in the domestic energy mix, the European debate on 2030 energy and climate targets and Japan’s discussions on a new energy plan), fossil sources still account for most of the global energy supply. It is also foreseen that energy-related $CO_2$ emissions will have risen 20% by 2035 (OECD/IEA, 2013).

Amongst the numerous measures adopted in order to contrast this issue, it is worth mentioning the Carbon Capture and Storage (CCS) technology. It allows to capture up to 90% of the carbon dioxide emissions produced from the use of fossil fuels in electricity generation and industrial processes, preventing the carbon dioxide from entering the atmosphere. As a result, the use of CCS may contribute to reducing carbon dioxide emitted into the atmosphere, while in the meantime further research can be developed in order to meet the zero emission target (Herzog et al., 1997; IPCC, 2005; MIT, 2007; Mazzella, 2011). Another method to scale down carbon emissions is $CO_2$ Geological Sequestration (CGS). According to it, $CO_2$ is stored in underground geologic formations (Pruess and García, 2002; Doughty et al., 2004; Juanes et al., 2006; Bachu et al., 2007; Class et al., 2009; Xu et al., 2011; Zhang and Bachu., 2011; Mazzella, 2011).

Evidently, carbon dioxide accumulates in the atmosphere, strengthening the natural greenhouse effect and resulting in global warming, for the environment cannot balance in the short term the significant increase in $CO_2$. It has been reported that each of the last three decades has been successively warmer at the Earth's surface than any preceding decade since 1850 (IPCCa, 2013). Were this trend not to reverse, humankind would have to face serious threats to the environment, caused by further global warming and changes in all components of the climate system.

Climate change is the most significant outcome of this, not to mention the consequences on nature and the animals. A case in point could be the increasingly rapid melting of glaciers and the subsequent sea level rise, which may impinge on aquatic ecosystems and the life of wild animals (including penguins and polar bears), as well as built-up environments such as urbanised areas that are few metres above sea level. Besides, other crucial climatic modifications are predicted to occur, such as a growth in the frequency and intensity of precipitation and increases in intensity of drought and in cyclone activity (Figure 2).

Additionally, serious implications of the peak in carbon emissions are related to urban environments. As a result of the production of heat from air conditioning systems, industrial processes and motor traffic, it appears that in built-up areas the average temperature is higher than that of the rural areas. Thus, a growing number of people are liable to be affected by heat-waves[1] and, moreover, exposed to unhealthy levels of air pollution.

Even though some of the causes of the increase in atmospheric $CO_2$ are related to anthropogenic activities that are strictly necessary, such as those industrial or energy-related, it is of the utmost importance to act so as to mitigate negative impacts that might arise both in the short and in the long run.

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[1] A period of abnormally and uncomfortably hot weather (Glossary IPCCa, 2013)

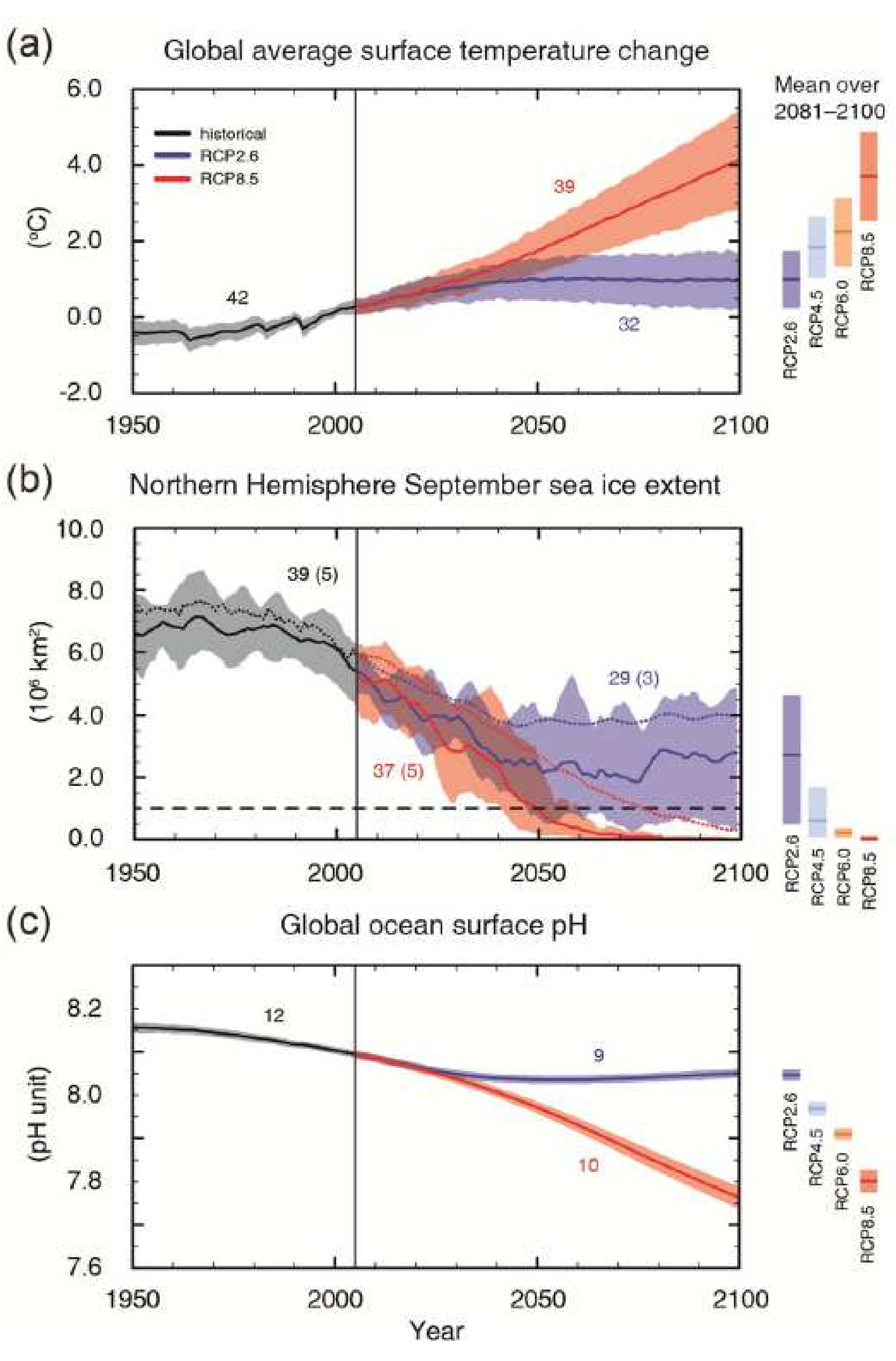

**Figure 2.** Effect of greenhouse gases emissions on some components of the climate system (IPCCb, 2013)

### *Lime and Cement Industry as the Major Industrial Producers of Carbon Dioxide*

Cement is a major construction material, used approximately worldwide. Cement-based materials are constantly manufactured and predicted to be used not only in the near but also in the far future. However, cement and mortar production is an industrial processes releasing impressive amounts of $CO_2$ into the atmosphere (Rehan and Nehdi, 2005; Rodrigues and Joekes, 2011). Portland cement production is responsible for 7% (2.1 x$10^9$ tons) of annual human carbon dioxide emissions, principally due to the production of cement clinker, which is the binder part of cement, mainly composed of limestone and alumino-silicates (IEA-WBCSD, 2009). Portland clinker stems from the calcination reaction of limestone (1), according to which calcium carbonate ($CaCO_3$) is converted into calcium oxide (i.e. lime - CaO) and carbon dioxide: as a result, it has been estimated that 1 kg cement Portland clinker production releases about 0.87 kg of $CO_2$ into the atmosphere (WBCSD-CSI, 2009).

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

Furthermore, also lime industry is involved in this process, since calcination occurs in the production of natural hydraulic lime as well. In fact, natural hydraulic limes (NHLs) are produced by calcining argillaceous or siliceous limestones at around 1200°C, whereas cement clinker production requires higher temperatures, namely about 1450°C.

Nevertheless, it is widely known that a percentage of emitted $CO_2$ due to the production of NHLs and cement-based products is reabsorbed during mortar setting and hardening, thanks to carbonation reactions (2) (3) (Moorehead, 1986), by means of which the $CO_2$ reacts with calcium hydroxide ($Ca(OH)_2$) in mortars and precipitates as calcium carbonate.

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (2)$$

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \ + 74\ kJ/mol \qquad (3)$$

Therefore, carbonation in lime and cement products can be regarded as a $CO_2$ “sink”, that is a process that removes $CO_2$ from the atmosphere and stores it (Rehan and Nehdi, 2005). Other $CO_2$ sinks are oceans, forests and agricultural soils, which are, indeed, natural elements.

Literature on carbonation of cement-based products (i.e. mortars and concrete) has been mainly concentrated on degradation (Roy and Poh, 1999; Song and Kwon, 2007). This stems from the reaction between alkaline compounds such as calcium hydroxide and calcium silicate with $CO_2$ present in the atmosphere, producing water and the precipitation of calcium carbonate. Usually, the alkaline compounds confer to pore water solution a pH above 13, which chemically protects steel reinforcement in concrete from corroding; however, carbonation provokes a sink in the pH due to the intrusion of $CO_2$, altering the passive conditions of steel bars, which consequently corrode and increase in volume, thereby causing microcracking and a decrease in porosity (Johannesson and Utgenannt, 2001; RILEM, 2007; L. Massidda, 2011).

Although scientific literature concerning accelerated carbonation of coal ashes (Jo et al, 2012), alkaline industrial waste residues (i.e.: steel slag, fly ash, cement kiln dust, waste cement, etc.) (Huntzinger et al., 2009; Cappai et al., 2013), sludge from urban waste water treatment plants (Valls and Vazquez, 2001), and soils and sludge including numerous metal pollutants (Fernández Bertos et al., 2004) is plentiful, little research has been conducted concerning the positives of the application of carbonation technology on cement- and/or lime-based materials. Nonetheless, a secondary effect of carbonation is the uptake of atmospheric $CO_2$. It should be pointed out, however, that in this process only the $CO_2$ emitted from the carbonation of limestone (which accounts for 50% of total emission) can be considered, leaving out the $CO_2$ emitted from energy related processes (Rehan and Nehdi, 2005). In fact, $CO_2$ release in cement plants also occurs during the burning of fossil fuels, in the transport activities and in the electricity supply.

Whilst literature on carbonation of concrete mainly focuses on negative effects which lead to its degradation, which principally involves corrosion and passivation of steel reinforcement, lime and cement mortars are not subjected to rebar corrosion having not structural use (Van Balen, 2005; Cultrone et al., 2005; Cizer et al., 2012).

Given that every year cement and lime industry provokes a considerable amount of world's $CO_2$ emissions (Mehta, 2002; Pade et al., 2007; Yilmaz et al., 2007; Celik et al., 2014), it is interesting to understand which part of these emissions could be re-absorbed through carbonation in the so-called “ecological mortars” object of this study, namely cement- and lime-based materials made from stone waste. The objective of this part of the study is to evaluate the amount of $CO_2$ taken up by lime and cement mortars under ordinary environmental conditions. To this purpose, the $CO_2$ sequestration capacity during the setting and hardening in the first 28 days of the “ecological mortars” was evaluated. Although $CO_2$ sequestration figures are far from the performance of other materials (such as coal ash and industrial residues), mortars have great potential, since their use in all built-up environments is impressively widespread.

*Technical Work and Subdivision into Activities*

Firstly, a broad analysis of the International Stone Sector was performed, in order to quantify quarry production trends and to evaluate the amounts and the different typologies of waste. Generally, the processed quarrying production accounts for a minor part of total stone extracted, whilst waste (quarrying waste and processing waste) amounts to the majority of total stone extracted. Additionally, world's main producers and the trend of quarrying and dimension stone exports were investigated. Afterwards, an overview of the legislation on natural stone waste, a study about the different waste typologies, and an investigation on current re-uses of stone waste were conducted. The conclusions of this preliminary study are the following: not only could coping with waste be environmentally damaging, but it is also economically expensive for the stone industry, which in addition has to deal with the economic loss caused by the lower efficiency of quarrying. Some re-uses of natural stone waste, such as the production of aggregates, have already been investigated, but they are not profitable for most quarrying companies. After having carried out the preliminary studies, the production of mortars (mixtures of cement, fine aggregates and water) has been identified amongst the possible uses as the most suitable one, since stone waste can be re-used to some extent as a substitute of the cement fraction and for the production of the aggregate fraction, thus obtaining a higher re-use rate.

After this preliminary phase, a more technical work was initiated. Initially, the stone waste object of this study was supplied by a quarrying company which is member of the Orosei Marble District (N-E Sardinia, Italy). Physical, chemical and mineralogical characterization of the natural stone waste was performed. All concentrations of hazardous elements are below legislation limits[2]. Therefore, the absence of pollutants highlighted that the re-use of these materials is suitable for commercial purposes.

Subsequently the “ecological mortars” were manufactured, by producing a number of experimental mix-designs and using the different fractions of stone waste previously collected.

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[2] D.M. Ambiente 5 aprile 2006, n.186: Regolamento recante modifiche al decreto ministeriale 5 febbraio 1998 «Individuazione dei rifiuti non pericolosi sottoposti alle procedure semplificate di recupero»; D.M. Ambiente 27 settembre 2010: «Definizione dei criteri di ammissibilità dei rifiuti in discarica, in sostituzione di quelli contenuti nel decreto del Ministro dell'ambiente e della tutela del territorio 3 agosto 2005» [*Italian Decree April 5, 2006, no. 186: Regulation amending Ministerial Decree February 5, 1998 «Identification of non-hazardous waste subject to simplified recovery procedures»; Italian Decree September 27, 2010: «Definition of the criteria for acceptance of waste in landfills, replacing those contained in the Decree of the Minister of Environment and Protection of Land August 3, 2005»*].

Afterwards, in order to further enhance the environmental advantages of re-using stone waste for the production of mortars, the $CO_2$ sequestration capacity of the “ecological mortars” was investigated in this research. After defining the experimental procedures (using a volumetric approach according to Ciccu et al., 2011; Mazzella et al., 2012) the parameters influencing the reaction were pointed up in order to quantify the amount of carbon dioxide absorbed during mortar setting and hardening.

The first step was to select two commercial mortars constituted of carbonate materials (high percentage of $CaCO_3$), as well as the waste object of the research. The first one is a cement mortar (EN 998-1:2003), which is suitable for new buildings and reinforced concrete, while the second one is a natural hydraulic lime mortar (EN 459-1:2010), suitable for ancient masonry buildings. Then, the assessment of the $CO_2$ uptake of the commercial mortars through experimental tests was performed, in order to establish a set of parameters to which compare the performance of the “ecological mortars”, in other words the mortars constituted by stone waste.

Secondly, several fresh mix-designs of the “ecological mortars” were manufactured with a percentage of the stone waste object of this study as a constituent. As well as the commercial mortars, they underwent the experimental procedure in order to evaluate their $CO_2$ consumption. Furthermore, the comparison between the $CO_2$ sequestration of the commercial mortars previously studied and that of the “ecological mortars” was drawn.

The experimental results showed that both the commercial mortars and the “ecological mortars” are capable to absorb $CO_2$. Even though the former mixtures showed higher uptake figures, after the first 28-day curing period they flattened out. On the contrary, the “ecological mortars” reported an uptake that was on the increase, hinting at the fact that there is room for further carbonation after the first 28-day period, thus the chance of higher sequestration considering a longer curing period.

These values could indeed represent a significant contribution in dealing with the the reabsorption of carbon dioxide emissions, by considering the entire service life of mortars.

As a result of this work, the “ecological mortars” are assigned a further environmental value of sequestration of one of the most polluting atmospheric gas, carbon dioxide, in addition to their being by-products made from waste which would be dumped in landfills instead.

## *References*

Aukour F. J., Al-Qinna M. I. (2008). Marble Production and Environmental Constrains: Case Study from Zarqa Governorate, Jordan, Jordan Journal of Earth and Environmental Sciences 1(1), 11-21.

Bachu S., Bonijoly D., Bradshaw J., Burruss R., Holloway S., Christensen N.P., Mathiassen O.M., (2007). $CO_2$ storage capacity estimation: Methodology and gaps, International journal of greenhouse gas control 1, 430–443.

K. Celik, M.D. Jackson, M. Mancio, C. Meral, A.-H. Emwas, P.K. Mehta, and P.J.M. Monteiro, High-volume natural volcanic pozzolan and limestone powder as partial replacements for portland cement in self-compacting and sustainable concrete (2014). Cement and Concrete Composites 45, 136–147.

R. Ciccu, A. Mazzella, C. Tilocca and G. Mei (2011). $CO_2$ uptake and metal release capacity of carbonated Sulcis Coal Ash, Proceedings Sardinia 2011, Thirteenth International Waste Management and Landfill Symposium S. Margherita di Pula, Cagliari, Italy; 3 - 7 October 2011, CISA Publisher, Italy.

Ö. Cizer, K. Van Balen, J. Elsen and D. Van Gemert (2012). Real-time investigation of reaction rate and mineral phase modifications of lime carbonation, Construction and Building Materials 35, 741–751.

H. Class, A. Ebigbo, R. Helmig, H. K. Dahle, J. M. Nordbotten, M. A. Celia, P. Audigane, M. Darcis, J. Ennis-King, Y. Fan, B. Flemisch, S. E. Gasda, M. Jin, S. Krug, D. Labregere, A. Naderi Beni, R. J. Pawar, A. Sbai, S. G. Thomas, L. Trenty, L. Wei (2009). A benchmark study on problems related to $CO_2$ storage in geologic formations, Computational Geosciences, 13 (4), 409-434.

V. Corinaldesi, G. Moriconi, T.R. Naik (2010). Characterization of marble powder for its use in mortar and concrete, Construction and Building Materials 24, 113–117.

G. Cultrone, E. Sebastián, and M. Ortega Huertas (2005). Forced and natural carbonation of lime-based mortars with and without additives: Mineralogical and textural changes, Cement and Concrete Research 35, 2278– 2289.

D.M. Ambiente 5 aprile 2006, n.186: Regolamento recante modifiche al decreto ministeriale 5 febbraio 1998 «Individuazione dei rifiuti non pericolosi sottoposti alle procedure semplificate di recupero» *[Ministry of Environment - Italian Decree April 5, 2006, no. 186: Regulation amending Ministerial Decree February 5, 1998 «Identification of non-hazardous waste subject to simplified recovery procedures»].*

D.M. Ambiente 27 settembre 2010: «Definizione dei criteri di ammissibilità dei rifiuti in discarica, in sostituzione di quelli contenuti nel decreto del Ministro dell'ambiente e della tutela del territorio 3 agosto 2005» *[Ministry of Environment - Italian Decree September 27, 2010: «Definition of the criteria for acceptance of waste in landfills, replacing those contained in the Decree of the Minister of Environment and Protection of Land August 3, 2005»].*

C. Doughty, K. Pruess, S. M. Benson, B. M. Freifeld, Barry M., and W. D. Gunter (2004). Hydrological and geochemical monitoring for a CO2 sequestration pilot in a brine formation. LBNL Report 55104, Lawrence Berkeley National Laboratory, Berkeley, CA.

European Aggregates Association [UEPG] (2009). “Annual review 2008-2009”, UEPG aisbl, Brussels.

2000/532/EC: Commission Decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste (notified under document number C(2000) 1147) (Text with EEA relevance)

M. Fernández Bertos, S.J.R. Simons, C.D. Hills and P. J. Carey (2004). A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of $CO_2$, Journal of Hazardous Materials B 112, 193–205.

H.J. Herzog, E.M. Drake, E.E. Adams (1997). $CO_2$ capture, reuse, and storage technologies for mitigating global climate change. Final Report, DOE No. DE-AF22- 96PC01257, Massachussets Institute of Technology, Cambridge, MA, 1997, pp. 66.

D.N. Huntzinger, J.S. Gierke, S.K. Kawatra, T.C. Eisele, L.L. Sutter (2009). Carbon dioxide sequestration in cement kiln dust through mineral carbonation, Environmental Science & Technology 43, 1986–1992.

IEA-WBCSD (2009). “Cement Technology Roadmap 2009 – Carbon emissions reductions up to 2050” - available at: www.wbcsd.org.

International Union of Laboratories and Experts in Constructions Materials, Systems and Structures [RILEM] (2007). Proceedings pro056: International RILEM Workshop on Integral Service Life Modelling of Concrete Structures, edited by R. M. Ferreira, J. Gulikers, C. Andrade, 1-458.

Intergovernmental Panel on Climate Change [IPCC] (2005). “IPCC Special Report on Carbon Dioxide Capture and Storage”. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCCa. Intergovernmental Panel on Climate Change [IPCC] (2013). “Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change”, [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and

P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp - available at: http://www.climatechange2013.org/.

IPCCb.Intergovernmental Panel on Climate Change [IPCC] Working Group I Contribution to the IPCC Fifth Assessment Report - “Climate Change 2013: The Physical Science Basis. Summary for Policymaker” (2013) - available at: http://www.climatechange2013.org/.

H. Y. Jo, J. H. Kim, Y. J. Lee, M. Lee, and S.-J. Choh (2012). Evaluation of factors affecting mineral carbonation of $CO_2$ using coal fly ash in aqueous solutions under ambient conditions, Chemical Engineering Journal 183, 77– 87.

B. Johannesson and P. Utgenannt (2001). Microstructural changes caused by carbonation of cement mortar, Cement and Concrete Research, 31 (6), 925–931.

R. Juanes, E. J. Spiteri, F. M. Orr Jr. and M. J. Blunt, (2006). Impact of relative permeability hysteresis on geological $CO_2$ storage, Water Resources Research 42 W12418, doi:10.1029/2005WR004806.

G. Marras (2010). “Recovery and valuation of ultrafine marble dust contained in waste slurries deriving from carbonatic natural stones processing plants”, thesis of the Geoengineering and Environmental Technologies Ph.D., University of Cagliari, Cagliari.

L. Massidda (2011). Le cause di degrado del calcestruzzo e delle opere in calcestruzzo armato, Enco Journal 53 - available at: http://www.enco-journal.com/journal/ej53/massidda.html

A. Mazzella (2011). “Studio preliminare per la valutazione della fattibilità di un progetto di CO2-ECBM nel bacino carbonifero del Sulcis”, thesis of the Geoengineering and Environmental Technologies Ph.D., University of Cagliari, Cagliari.

A. Mazzella, C. Tilocca, R. Ciccu, and G. Mei (2012). Capacità di assorbimento della CO2 e di rilascio dei metalli pesanti delle fli-ash del carbone "Sulcis", Resoconti della Associazione Mineraria Sarda Iglesias, Anno CXIV-CXVII 2009-2012.

P.K. Mehta (2002). Greening of the concrete industry for sustainable development, Concrete International, 24, 23.

MIT (2007). “The future of coal. Options for a carbon-constrained world. An interdisciplinary MIT study”. Massachusetts Institute of Technology.

D. R. Moorehead, (1986). Cementation by the carbonation of hydrated lime, Cement and Concrete Research 16, 700-708.

Organization for Economic Co-operation and Development [OECD] and International Energy Agency [IEA] (2008). “World energy outlook 2008”, IEA Publications, Paris - available at: http://www.worldenergyoutlook.org.

Organization for Economic Co-operation and Development [OECD] and International Energy Agency [IEA] (2013), “World energy outlook 2013”, IEA Publications, Paris - available at: http://www.worldenergyoutlook.org.

C. Pade and M. Guimaraes (2007). The $CO_2$ uptake of concrete in a 100 year perspective, Cement and Concrete Research 37, 1348–1356.

K. Pruess and J. García (2002). Multiphase flow dynamics during $CO_2$ injection into saline aquifers, Environmental Geology 42, 282-295.

R. Rehan, M. Nehdi (2005). Carbon dioxide emissions and climate change: policy implications for the cement industry, Environmental Science & Policy 8, 105–114.

F. A. Rodrigues, I. Joekes (2011). Cement industry: sustainability, challenges and perspectives, Environmental Chemistry Letters 9 (2), 151–166.

S.K. Roy, K.B. Poh and D.O. Northwood (1999). Durability of concrete-accelerated carbonation and weathering studies, Building and Environment 23, 597-606.

Sardegna Ricerche and Consorzio 21 (2002). “Natural Stone from Sardinia. Technical Handbook”, Sardegna Ricerche, Cagliari.

H. Song and S. Kwon (2007). Permeability characteristics of carbonated concrete considering capillary pore structure, Cement and Concrete Research 37, 909–915.

T. Stocker and Q. Dahe - IPCC Working Group I, “Overview of the IPCC WGI Report” (2013) - available at: http://www.climatechange2013.org/.

S. Valls and E. Vazquez (2001). Accelerated carbonation of sewage sludge–cement–sand mortars and its environmental impact, Cement and Concrete Research 31, 1271-1276.

K. Van Balen (2005). Carbonation reaction of lime, kinetics at ambient temperature, Cement and Concrete Research 35, 647– 657.

WBCSD-CSI (2009). Cement Industry Energy and $CO_2$ Performance “Getting the Numbers Right”. Washington, DC - available at: www.wbcsdcement.org.

T. Xu, L. Zheng and H. Tian (2011). Reactive transport modeling for $CO_2$ geological sequestration, Journal of Petroleum Science and Engineering 78 (3–4), 765–777.

B. Yilmaz, A. Uçar, B. Öteyaka, and Uz V. (2007). Properties of zeolitic tuff (clinoptilolite) blended portland cement, Building and Environment 42 (2007) 3808–3815.

M. Zhang and S. Bachu (2011). Review of integrity of existing wells in relation to CO2 geological storage: What do we know?, International Journal of Greenhouse Gas Control 5 (4), 826–840.

# Chapter 1. The International Stone Sector

## *1.1 Overview of the international dimension stone sector*

### *1.1.2 Object of the study: background information about commercial marbles*

As aforementioned, dimension stones are natural rock materials quarried so as to meet standards set for commercial purposes. The most important dimension stones produced in the world in terms of market size are currently commercial marbles and granites, respectively ascribable to the calcareous and to the siliceous stone typologies. Production of marble is greater than that of granite, which results in huge quantities of waste produced. For this reason, marble, and more specifically commercial marbles, have been chosen for further investigation.

Marble is a stone of metamorphic origin. It derives from metamorphosed limestone, which after being exposed to high temperatures and pressure is reformed into an interlocking structure of calcite, dolomite or a combination of both minerals. Furthermore, commercial marbles may include any other stone composed of calcium carbonate that takes polish, such as limestone itself or travertine. Although they are sedimentary rocks, they are mainly composed of calcium carbonate as well as marble. This implies that the term “commercial marble” extracted for the dimension stone market commonly refers to both metamorphosed marble and sedimentary limestone, even though they come from different rock typologies. Also, this term tends to be extended to other stones containing calcium carbonate, such as onyx, alabaster, serpentine, etc. Therefore, henceforth when referring to “commercial marble” or “calcareous stone” in this work, these rock typologies will be taken into consideration.

Commercial marbles are usually sized into blocks, slabs, and tiles and mainly used for the production of rough blocks for building and construction, flagstone, curbing, ashlars and partially squared pieces, and monumental and memorial stones (Dolley, 2000). Other applications of these stones are related to the industrial sector. In fact, fine calcium carbonate powder, which can be obtained by grinding marble or other types of calcareous stones, is used in the paper industry, in plastics, in paints, in the pharmaceutical and cosmetic fields, and so on.

### *1.1.3 Notes on the dimension stone market at the international level*

Taking into consideration the global natural stone sector, an analysis of production at the international level has been carried out, focusing on its economic and quantitative significance. Data processing from different sources (Montani, 2011; USGS, 2011; UN Commodity Trade

Statistics Database, 2012) was undertaken, so as to include and compare data about production, consumption, and imports and exports in the dimension stone sector.

Firstly, the production of the main typologies of dimension stone has been considered, and the trend in time of the calcareous stone, the subject of this study, has been compared with that of siliceous stone.

**Table 1.1** World raw production of dimension stones, by main typologies, thousand cubic meters, years 2003-2010.

| | **Calcareous stone** | **Siliceous stone** | **Other types of stone** | **% of calcareous stone** | **% of siliceous stone** | **% of other stones** | **Total output** |
|---|---|---|---|---|---|---|---|
| **2003** | 15,741 | 10,556 | 1,481 | 56.7 | 38.0 | 5.3 | 27,778 |
| **2004** | 16,204 | 12,222 | 1,667 | 53.8 | 40.6 | 5.5 | 30,093 |
| **2005** | 17,315 | 12,593 | 1,667 | 54.8 | 39.9 | 5.3 | 31,574 |
| **2006** | 19,759 | 12,889 | 1,704 | 57.5 | 37.5 | 5.0 | 34,352 |
| **2007** | 22,407 | 13,889 | 2,037 | 58.5 | 36.2 | 5.3 | 38,333 |
| **2008** | 22,593 | 14,185 | 2,111 | 58.1 | 36.5 | 5.4 | 38,889 |
| **2009** | 22,537 | 14,074 | 2,093 | 58.2 | 36.4 | 5.4 | 38,704 |
| **2010** | 24,159 | 15,000 | 2,130 | 58.5 | 36.3 | 5.2 | 41,289 |
| **2003-2010 variation** | 8,419 | 4,444 | 648 | 2 | -2 | -0.1 | 13,511 |

From Table 1.1 and Figure 1.1, it is possible to note that currently the trend of production of dimension stones is rising.

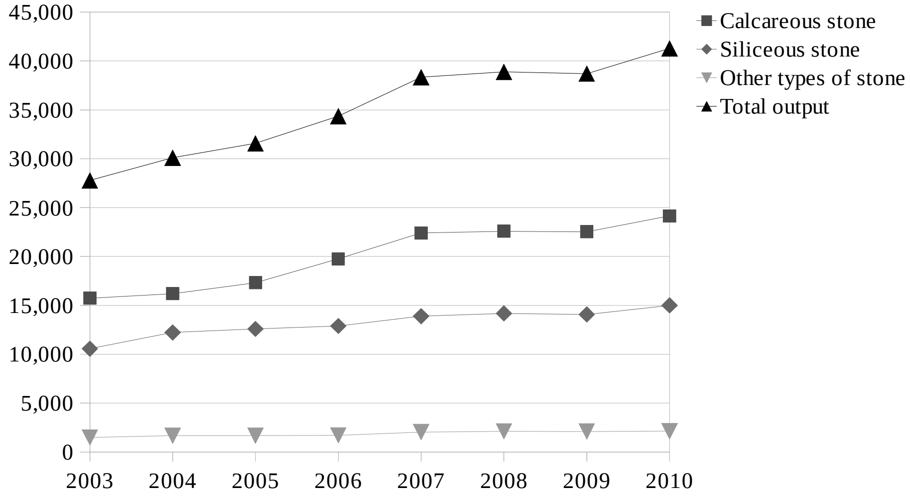

**Figure 1.1.** World raw production of dimension stones, by main typologies, thousand cubic meters, years 2003-2010.

Moreover, not only does calcareous stone account for more than a half of the world raw production of dimension stones, but also the overall output of this typology has increased over the whole period taken into consideration, despite a decline in the 2007-2009 period, which, however, has been critical for each typology.

Before considering the absolute production values, attention will be concentrated on the mean annual variations in the raw production for calcareous and siliceous stones for the period from 2003 to 2010, which is the latest year for which data are available (Table 1.2).

This period was subdivided into seven intervals, each corresponding to a year. In this way, some important differences between the main stone typologies may be highlighted. Firstly, while at the beginning, from 2003 to 2004, the trend of siliceous stone was higher than that of calcareous stone, afterwards the performance of calcareous stone was superior. On the other hand, from 2007 an overall crisis for the sector occurred, resulting in more critical consequences for calcareous stone, which reports a more significant decrease than that of siliceous stone.

**Table 1.2**. Comparison of mean annual variations in global raw production of dimension stones, by main typologies, years 2003-2010.

| | **Calcareous stone** | **Siliceous stone** | **Other types of stone** | **Total output** |
|---|---|---|---|---|
| **Period of time** | *mean annual variation* | *mean annual variation* | *mean annual variation* | *mean annual variation* |
| **2003-2004** | 463 | 1,667 | 185 | 2,315 |
| **2004-2005** | 1,111 | 370 | 0 | 1,481 |
| **2005-2006** | 2,444 | 296 | 37 | 2,778 |
| **2006-2007** | 2,648 | 1,000 | 333 | 3,981 |
| **2007-2008** | 185 | 296 | 74 | 556 |
| **2008-2009** | -56 | -111 | -19 | -185 |
| **2009-2010** | 1,622 | 926 | 37 | 2,585 |

This crisis continued until 2009, which is a year with even negative variation values, both for each stone typology and the total output. Actually, the sharp decline in calcareous stone production has little importance owing to the fact that it corresponds to the general trend of the sector. In fact, since 2009 calcareous stone has increased dramatically. Also, it is noticeable from data reported that calcareous stone has a predominant role in the total output of dimension stones: when the average production of calcareous stone increases, total output increases as well. This is mainly due to the fact that the production of calcareous stone over the period considered (2003-2010) was in the region of 60% of the world raw production of dimension stones. To conclude, after a period of crisis, the 2009-2010 period saw renewed growth for the natural stone sector, with higher production and higher trends for calcareous than siliceous stone.

Global production, the trend in time, and the amount of natural stone waste coming from the dimension stone sector can be seen below. In Table 1.3 the world production of dimension stones for the period 2003-2010 is reported, and subdivided into gross and raw production. The latter corresponds to the total output shown in previous tables. In fact, the total raw output of dimension stone can be obtained by subtracting waste from the gross quarrying output.

**Table 1.3.** World production of dimension stones, thousand cubic meters, years 2003-2010.

| | Gross quarrying | Quarrying waste | Raw production | Processing waste | Processed production | Processed production as a % of gross quarrying | Total production of stone waste | Total waste production as a % of gross quarrying |
|---|---|---|---|---|---|---|---|---|
| **2003** | 57,000 | 29,222 | 27,778 | 11,400 | 16,400 | 29 | 40,622 | 71 |
| **2004** | 61,650 | 31,557 | 30,093 | 12,300 | 17,800 | 29 | 43,857 | 71 |
| **2005** | 64,750 | 33,176 | 31,574 | 12,950 | 18,650 | 29 | 46,126 | 71 |
| **2006** | 70,450 | 36,098 | 34,352 | 14,100 | 20,250 | 29 | 50,198 | 71 |
| **2007** | 78,500 | 40,167 | 38,333 | 15,750 | 22,550 | 29 | 55,917 | 71 |
| **2008** | 79,600 | 40,711 | 38,889 | 15,950 | 22,950 | 29 | 56,661 | 71 |
| **2009** | 79,150 | 40,446 | 38,704 | 15,900 | 22,800 | 29 | 56,346 | 71 |
| **2010** | 84,450 | 43,161 | 41,289 | 12,350 | 28,950 | 34 | 55,511 | 66 |

Figure 1.2 shows the trends of gross, net and waste production, which give an indication of the general efficiency of the dimension stone quarries.

From the Figure 1.2, it can be seen that the processed production, which expresses the final product of the quarrying industry, is actually a rather low percentage of the total volume extracted. In fact, it is at around 30% of the gross quarrying. On the contrary, the total production of stone waste, accounting for both the quarrying waste and the processing waste, is still the largest output of this sector, reaching about 70% of total volume extracted.

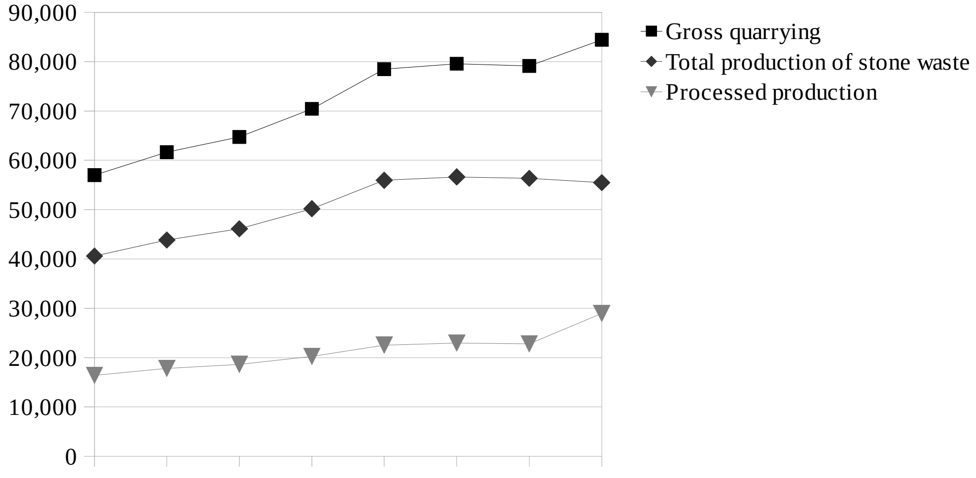

**Figure 1.2.** World production of dimension stones, thousand cubic meters, years 2003-2010.

On the other hand, taking the trends into consideration, over the last period covered (2009-2010) there was a positive slope of the processed production curve, whereas the production of stone waste curve had a relative decline, meaning that a decrease in production of stone waste in favor of an increase in processed production had occurred.

This is mainly due to the quarrying companies’ efforts to increase quarry efficiency and the gradual improvement of quarrying techniques. However, this trend is quite recent. Figure1.2 shows that up to 2007 the waste curve had followed step by step the production curve. Moreover, the absolute value of the production of waste is still far superior to the processed production. Therefore, it is still necessary to strive to improve the efficiency of quarrying activity. In an ideal situation, the best result can be achieved by means of the total re-use of waste materials, but there is still a mainstream tendency to consider natural stone waste as run-out materials rather than secondary resources. The huge production of dimension stone waste can still lead to negative environmental consequences. It should be noted that the enormous waste output over the past years has given rise to a massive accumulation of materials that lie in quarry areas or landfills, creating considerable environmental issues.

The world's producers of dimension stone were considered in order to identify the top producers and their production trends. From the data reported in Tables 1.4 and 1.5, it can be seen that currently the world’s main producers are China and India. The trend of quarrying and dimension stone production has decreased over recent years for major producers of Western Countries (Italy, Spain, and Portugal), whereas it is currently growing for some of the BRIICS Countries (China, India, and Brazil).

As regards the Western countries, Italy, in particular, has had for centuries a predominant role in the natural stone industry. Also, it has an ancient tradition of quarrying and dimension stone exports. However, as a result of new countries (China, India, Iran and others) entering the world stone sector, Italy has gradually lost its first place in the list of the world’s main producers of dimension stone. Over the last decades, China has risen into the top ten in the production of dimension stones, reaching the top position. With reference to the period considered (2003-2010), the year 2010 marked a further contraction in Italian production, which fell to fifth place.

**Table 1.4.** Top world producers of dimension stones, thousand cubic meters, years 2003 and 2010 (Guide to the mining industry and to recycling, 2002; Montani, 2011).

| | **2003** | | | **2010** | | | |
|---|---|---|---|---|---|---|---|
| | **Country** | **Production** | **Share** | **Country** | **Production** | **Share** | **Rank variation** |
| **1** | China | 6,481 | 23.3 | China | 12,222 | 29.4 | *stable* |
| **2** | India | 3,148 | 11.3 | India | 4,907 | 11.9 | *stable* |
| **3** | Italy | 2,907 | 10.5 | Turkey | 3,704 | 9.0 | *new entry* |
| **4** | Spain | 2,130 | 7.7 | Iran | 3,148 | 7.6 | *up (+1)* |
| **5** | Iran | 1,796 | 6.5 | Italy | 2,889 | 7.0 | *down (-2)* |
| **6** | Brazil | 1,185 | 4.3 | Brazil | 2,500 | 6.1 | *stable* |
| **7** | Portugal | 833 | 3.0 | Spain | 2,130 | 5.2 | *down (-3)* |
| **8** | USA | 833 | 3.0 | Portugal | 1,019 | 2.5 | *down (-1)* |
| **9** | Greece | 537 | 1.9 | USA | 685 | 1.7 | *down (-1)* |
| **10** | France | 463 | 1.7 | Greece | 611 | 1.5 | *down (-1)* |
| | Others | 7,463 | 26.8 | Others | 7,481 | 18.1 | - |
| | **World** | **27,778** | **100** | **World** | **41,296** | **100** | - |

**Table 1.5.** Comparison between Italy and China's performance.

| | **China** | | **Italy** | | **World** | |
|---|---|---|---|---|---|---|
| | *Production (thousand cubic meters)* | *World share (%)* | *Production (thousand cubic meters)* | *World share (%)* | *Production (thousand cubic meters)* | *Total* |
| **2003** | 6,481 | 23.3 | 2,907 | 10.5 | 27,778 | 100 |
| **2010** | 12,222 | 29.4 | 2,889 | 7.0 | 41,296 | 100 |
| **Variation** | **5,741** | **6.1** | **-19** | **-3.5** | **13,518** | **-** |

In particular, in Table 1.5 a comparison between the performance of China and Italy is reported. While Chinese production is steadily increasing, both for absolute values and world share, over the years considered the output of the Italian dimension stone sector with respect to world production has plummeted to 3.5 percent, although with a small contraction (-19 thousand cubic meters).

In conclusion, from the analysis it emerges that over the past decade the production of those Western countries with a longstanding tradition in the dimension stone sector (Italy, Spain, Portugal, and Greece) has dropped, whereas the performance of some emerging economies such as China, India, Turkey, Iran, and Brazil has been exploding. Also, the production trend of the former world leader (Italy) and the current leader (China) confirms this statement.

In Table 1.6 the data on the per capita consumption of dimension stone for some of the top world producers are reported in equivalent square meters, related to a conventional thickness of 2 cm (Montani, 2011), per 1000 inhabitants.

**Table 1.6.** Per capita consumption of dimension stone for some of the top world producers (sq.mt./2 x 1000 inhabitants), years 2003 – 2010 (data processing from Montani, 2011).

| | **China** | **India** | **Brazil** | **USA** | **Italy** | **Spain** | **Portugal** | **Greece** | **France** |
|---|---|---|---|---|---|---|---|---|---|
| | ***Country consumption*** | | | | | | | | |
| 2003 | 72 | 48 | 94 | 276 | 1,070 | 1,202 | 1,066 | 1,456 | 478 |
| 2004 | 87 | 53 | 114 | 280 | 1,070 | 1,173 | 1,075 | 1,431 | 479 |
| 2005 | 94 | 58 | 112 | 329 | 1,084 | 1,319 | 1,188 | 1,451 | 496 |
| 2006 | 98 | 63 | 129 | 362 | 1,102 | 1,174 | 1,182 | 1,439 | 522 |
| 2007 | 125 | 65 | 142 | 377 | 1,088 | 1,119 | 1,147 | 1,583 | 505 |
| 2008 | 137 | 76 | 225 | 297 | 1,113 | 1,021 | 1,102 | 1,426 | 480 |
| 2009 | 165 | 75 | 228 | 240 | 1,010 | 898 | 1,112 | 1,245 | 429 |
| 2010 | 206 | 79 | 232 | 251 | 1,055 | 1,006 | 1,018 | 1,073 | 482 |
| | ***World production ranking (2010)*** | | | | | | | | |
| | **1** | **2** | **6** | **9** | **5** | **7** | **8** | **10** | **11** |

This is the usual way in which dimension stone output is expressed, for this material is mainly commercialized in slabs and tiles. Current major producers of dimension stones, such as China, India, and Brazil, have high production and high total consumption. However, taking into account the per capita consumption, it is in the range of hundreds of square meters per 1000 inhabitants, which is much lower than that of past major producers in Western Countries, reported in the range of thousands of square meters per 1000 inhabitants. In particular, for European States such as Italy, Spain, and Portugal, there is a much higher per capita consumption than that of developing countries, even though in recent decades a decline in production and lower total consumption for each country has occurred. This is probably due to the different living conditions and to the long tradition of use of dimension stone in Western Countries. Furthermore, top producer countries have higher population densities, resulting in a lower per capita consumption than in Europe. Also, it is important to point out that normal practice in the dimension stone market is producing to order so as to minimize the risk of overstocking, which can result in the economic overexposure of quarrying companies. Therefore, we can assume that the volume of world consumption of dimension stones is very close to that of production.

Therefore, in developing countries an increase in the per capita consumption of dimension stones is foreseen as a result of further economic development. Likewise, although in Western Countries such as Europe and the USA there is lower population growth and an economic crisis that has recently led to a contraction in the natural stone market, there is still higher per capita consumption of dimension stones than in China and the developing countries. Moreover, the contributions of Central and Eastern Europe are estimated to become increasingly significant, in addition to those of Western Europe. In fact, since the consumption of natural stone is closely related to the economic performance of a country, which is measured as gross domestic product per capita (GDP/capita), if we assume that the new emerging EU Member States are increasing their economic output, in the near future this will result in an increase in the consumption of dimension stone. This will lead to an increase in the demand and consequently in the production of dimension stones even in the Western industrialized countries.

In conclusion, in the near future the demand for dimension stones is expected to increase in Asia, in developing countries and also in industrialized countries despite their slow economic growth.

### *1.2. Natural Stone Waste Framework*

In recent times, a good deal of legislation along with white papers and good practice lists on waste management have been produced in many countries all over the world. The sustainable use of natural resources has gradually become a crucial point, both in the industrialized (or developed) and in the industrializing (or developing) countries.

A brief review of the regulatory framework and policies dealing with waste for the European context, the United States, the emerging Asian countries, and the Middle East and North Africa region has been undertaken.

As regards the European context, at the international level great effort has been made by the European Union to establish a common legislative framework shared by the EU Member States. According to Article 1(a) of Directive 75/442/EEC, waste is defined as "any substance or object in the categories set out in Annex I which the holder discards or intends or is required to discard". The European Waste Catalogue (EWC) was established by Commission Decision 2000/532/EC. It replaced the Decision 94/3/EC, drawing up a list of wastes on the basis of Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC on hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.

The EWC aims to establish a common classification of waste. It provides 20 different codes, which are subdivided into several sub-codes. In the EWC, wastes classified as hazardous are marked with an asterisk (*) pursuant to Directive 91/689/EEC. Natural stone waste is included in the EWC under the code 01: "Wastes resulting from exploration, mining, quarrying, physical and chemical treatment of minerals". More specifically, it is included in the sub-code 01 04 "waste from physical and chemical processing of non-metalliferous minerals" in further categories such as waste gravel and crushed rocks, dusty and powdery waste, waste from stone cutting and sawing, and wastes not otherwise specified. According to the EWC, dimension stone waste is mainly harmless, since only materials under the code 01 04 07*, "wastes containing dangerous substances from physical and chemical processing of non-metalliferous minerals" are identified as hazardous. In fact, extraneous or dangerous substances largely come from residues of the treatment of the stone, such as iron or other metal residues coming from the cutting with diamond wire saws or chain saw cutting machines. In fact, since the original rock and natural stone waste derives from the same materials, the most evident difference between them is their physical condition. This means that for waste different sizes and very wide particle size distributions are expected, varying from larger and smaller blocks, to even smaller dust particles resulting from the industrial processing activities. Additionally, a reduction in particle size means a consequent increase in volume.

The EU Member States are currently trying to include the classification proposed by the EWC into their national legislation.

The EU Waste Framework Directive[3] is also worth mentioning. This quite recent directive includes the ideas expressed in the list above. In fact, the concepts of waste, recycling and recovery have been accurately defined, and waste prevention has been recognized as the highest priority since it provides the best overall environmental outcome (Article 4). Additionally, the fact that in some cases waste ceases to be waste and becomes a secondary raw material (so called "end-of-waste criteria") is clearly mentioned. Also, how to distinguish between waste and by-products is clarified, and by-products are considered as falling into the category of products, thus their exports should meet the requirements of EU legislation on the subject.

As far as the United States is concerned, the situation is variegated owing to differences in the legislation of the 50 states. In broad terms, the federal government sets policy and regulations for hazardous waste, whereas non-hazardous waste is dealt with at the state level.

Generally, US policies are in line with the European approaches described above. There is a waste management hierarchy, which sets as first priority the re-use of materials, and afterwards recycling, saving energy, and lastly, disposal, such as incineration or landfill.

The Resource Conservation and Recovery Act (RCRA)[4], which came into force in 1976, is the principal federal law related to waste, which sets the general guidelines for the waste management program. According to this Act, the material has to be first characterized in order to decide whether it is a waste, and then the question of whether it is hazardous should be considered. Moreover, this Act identifies the US EPA (Environmental Protection Agency) as the developer of a set of regulations implementing the RCRA, which are compiled annually and incorporated into the Code of Federal Regulations (CFR). This code contains the regulations for both non-hazardous solid

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[3] European Parliament and Council, Directive 2008/98/EC.

[4] Resource Conservation and Recovery Act, P.L. 94-580, 90 Stat. 2795, 42 U.S.C. § 6901 et seq., October 21, 1976.

waste and hazardous waste. Following the RCRA program, there are “exclusions” and “exemptions” on waste hazardousness. “Exclusion” means that the material considered is not a waste. This is the case of those materials assigned to re-use or recycling operations. Therefore, at the US federal level they are not waste at all. By contrast, "exemption" means that the waste considered is non-hazardous, so it is exempted from the federal hazardous waste regulations (RCRA - Subtitle C).

In the United States, natural stone waste is considered industrial and more specifically mining waste, which is categorized by the EPA as "special waste". Mining is part of the mining, quarrying, and oil and gas extraction (NAICS 2) sector. This sector includes metal mining and nonmetallic mineral mining and quarrying. The term mining is used in the broad sense to include quarrying, well operations, beneficiating (e.g., crushing, screening, washing, and flotation), and other preparation customarily performed at the mine site, or as part of mining activity. Mining waste can be either of solid consistency (i.e: rejected blocks or excessively small fragments of the original blocks; further information is available below) or in the form of the so-called “sludge”, which is defined by the RCRA as “any solid, semisolid or liquid waste generated from a municipal, commercial, or industrial wastewater treatment plant, water supply treatment plant, or air pollution control facility or any other such waste having similar characteristics and effects”. Like blocks and stone fragments, sludge is also considered “solid waste” according to the RCRA section 1004 (Karaca et al., 2012). Although industrial waste can be either hazardous or non-hazardous, natural stone waste has been exempted by the Mining Waste Exclusion from the Subtitle C of the RCRA, as aforesaid, and is therefore included in the non-hazardous solid wastes. In fact, Congress amended the RCRA (the Solid Waste Disposal Act Amendments, 1980) by exempting some kinds of waste from the definition of hazardous waste pending further study by the EPA. The exempted wastes include “solid waste from the extraction, beneficiation, and processing of ores and minerals, including phosphate rock and overburden from the mining of uranium ore” (the so-called “Bevill exclusion from Hazardous Waste Regulation”, RCRA added section 3001(b)(3)(A)(ii), 1980). These wastes were exempted because they were produced in very large volumes, were thought to pose less of a hazard than other wastes, and were generally not amenable to the management practices required under the RCRA. In particular, these policies are applied under the criteria of “large volume, low hazard” wastes.

Recently, rather weak waste management has become a crucial issue in Asian countries. Over the past decades, Asia's importance in world economic development has grown. In fact, a third of the global economy is handled in this region. Despite this, there is great variety in the economic and living conditions of people within Asian countries. “Asian countries” is a general term which comprises countries of close geographic location but with different economic output, grade of industrialization and percentage of urbanization with respect to rural areas. All these parameters may influence the production of waste. In addition to this, low income countries (e.g. Bangladesh, Cambodia and the Democratic People's Republic of Korea) as well as developing countries (e.g: India, Pakistan, Sri Lanka and Vietnam) and some among the world’s leading economies (China) are included in this geographic region, according to World Bank Analytical Classifications. With the exception of countries such as Japan and cities like Singapore and Hong Kong, municipal solid waste disposal sites are inadequate (UNEP, 1999). Also, the management of other types of waste such as industrial waste, whether hazardous or not, and municipal and industrial wastewater, is increasingly problematic. In fact, about 60% of industrial and hazardous waste is dumped in landfills, while up to 10% is dumped in the ocean, and the rest goes to either an incineration process or is chemically treated (Smith et al., 2000).

Usually, in low income countries, a high percentage (more than 80%) of the total waste management costs goes on collection. This is mainly due to the fact that disposal is the preferred option, owing to its lower cost with respect to incineration. There is indeed a widespread approach that considers the minimization of costs and their short term prevision (Parthan et al, 2012) as the main purpose of proper waste management, and the improvement of other important policies such as medium term planning and projections of financial costs is frequently neglected.

It is important to point out that some of the low income countries in Asia are actually emerging economies, or industrializing countries with growing economic output, an expected improvement in quality of life, and a high rate of urbanization progress. Since urban residents generate two to three times more solid waste than the rural population (Hassan, 2000; The World Bank, 1999), not only is the amount of solid waste expected to increase significantly, but also industrial, hazardous and liquid waste streams, leading to critical environmental issues. However, there is a general lack of awareness of the negative impact of waste, along with the perception that the possible solutions are too costly. The situation is currently improving, since governments, no-profit organizations, voluntary non-state organizations and foundations have been trying to deal with these issues, and also attempting to make people aware of the consequences of inefficient waste management by means of environmental education and communication.

Waste management is currently experiencing a deep change in the Middle East and North Africa. The economic growth of these countries, along with the considerable demographic growth, the migration to urban areas, improved living conditions and an improvement in the industrialization process have led to an increase in the amount of waste generated. Furthermore, a sharp increase in waste production has been predicted to occur in 2025, with average output of 77 million tons per year (Loukil and Rouachedb, 2012). In order to deal with this situation, countries in the region are trying to foster awareness of the impact of waste production among the communities, both from the environmental and the public health perspectives.

The main difficulties faced in this region are related to the development of the recycling approach, since waste disposal in landfills is generally preferred. Literature on the subject suggests that the recycling technique is broadly adopted in most industrialized countries, where it accounts for about 40% of waste treated, whereas in the Middle East and North Africa it is less than 10% of waste treated (Loukil and Rouachedb, 2012). This is mainly due to the fact that in developing countries there are a lot of landfills in urban areas, including open dumps. This could lead to possible harmful consequences. Additionally, disposal costs are usually very little high while public finances are limited. Frequently, civil organizations such as Community Based Organizations (CBOs) and Non-Governmental Organizations (NGOs) have a paramount role in coping with waste management in this region (Tukahirwa et al., 2013). Another significant issue is that in developing countries recycling by means of the informal sector is still widespread, that is the spontaneous waste recycling activities of scavengers and waste pickers (Wilson et al., 2006). Indeed, in developing countries a huge number of people depend on informal recycling for their livelihoods.

After having reviewed the regulatory frameworks on waste at the international level, it is possible to highlight some common features:

- the need for proper waste management in terms of waste prevention, re-use, material recycling, composting, recovery and final disposal. Recently, policies in this field have identified firstly waste prevention, and secondly the re-use and recycling of waste streams as the most desirable options, whereas their disposal is often not encouraged;
- the need to overcome the negative idea of waste and thus consider it as a resource to be used either in the same upstream activity or in different fields. On the contrary, in the past waste was frequently seen as useless, which led to its accumulation in great quantities that were potentially hazardous for the environment because of possible leaching, dust production, the visual impact on the landscape, and so on;
- the need for commonly accepted terminology on waste at the international level;
- the need for a clear classification of waste to enable clear distinctions as to whether particular waste typologies are harmful to human health and the environment or not;

- in the specific case of natural stone waste, the rising awareness that unused materials from the quarrying industry should not be considered as mere waste but as potential by-products of great economic interest;
- as for developing countries, in the near future the integration of the informal sector in waste management planning is strongly encouraged, rather than imposing a waste management model derived from that developed in the industrialized economies. Acting in this way, people who depend on informal recycling can both help the environment and maintain their livelihoods.

### *1.3 Types of wastes from quarrying activities and the current re-uses*

Despite the economic importance of the dimension stone industry, and also its crucial role as a source of employment all over the world, there is increasing public concern about its peculiarity of producing large amounts of natural stone waste.

Currently, this waste has great potential for re-use as a by-product in a number of industries, such as the pharmaceutical and chemical sectors and the manufacturing of paper and paints, which can utilize its mineral content (e.g: calcium carbonate, quartz, feldspar, and so on). Likewise, natural stone waste can be used in the agricultural field (Coroneos et al., 1996; Silva et al., 2012). Also, one of the first re-uses of dimension stone waste is in the same quarry, so as to create quarry slopes and embankments for future quarry reclamation. However, the construction industry is one of the most potentially interested sectors in the re-utilization of natural stone waste (Vieira et al., 2004; Menezes et al., 2005; Segadaes et al., 2005). In fact, it is reckoned to be one of the main consumers of mineral raw materials. The re-use of great amounts of solid waste as a by-product for the building industry could be a valuable solution to both the great demand for natural resources and the increasing issue of the disposal of huge quantities of natural stone waste.

Before going through possible solutions to natural stone waste disposal, it is necessary to examine the different typologies of waste. In fact, this waste stream may frequently occur at varied size and shape and also at different material states, either solid or liquid, providing different ranges of dimension and particle size.

Waste classification depends on the procedures adopted through the extraction process. In fact, we can split the production of dimension stone into two main processes: quarrying, in the strict sense of the word, and processing. Basically, quarrying consist of cutting out solid rock into large solid blocks with definite dimensions and sizes, whereas processing can be summarized as the activities of sawing, drilling and splitting into smaller final products which can be further subjected to surface finishing.

Both industrial processes raise different waste streams: quarrying waste and the processing waste. A review of the available literature on the subject suggest subdividing natural stone waste from quarrying activity into 3 main groups: (1) solid, (2) dust and (3) semi-slurry, slurry and cake (Almeida et al., 2007; Karaca et al., 2012).

Solid waste firstly comprises stone blocks that are unsuitable for the dimension stone market, which sells the so-called "first-grade blocks", slabs and tiles. Secondly, there are smaller pieces of waste. As regards the former, what usually occurs is that many blocks are rejected because of the presence of elements that alter their color and textural homogeneity, even if they have regular dimensions. They are called "second-" or "third-grade blocks". Also, there are "shapeless blocks", which have such irregular size and shape that cutting and sawing them further is either impossible or too costly.

Possible re-uses for second- or third-grade blocks are in civil engineering, in particular for civil works such as floors, external pavings, external wall facing, architectural details, etc. Shapeless blocks are generally used either for stabilization works, protecting walls, embankments or for the creation of squares within the quarry, in which quarry products are temporarily stocked or trucks are parked.

As regards smaller pieces of waste, they may derive either from stone fragments which have been rejected, for instance because of the presence of impurities or fractures, or from other materials left out after the valuable parts of the stone have been removed, owing to their small size. These pieces of waste are frequently re-used in the construction market for aggregates, either for concrete and concrete applications (Hebhoub et al., 2011; Gencela et al., 2012) or road materials (Rockliff, 1996; Akbulut and Gürer, 2007). In fact, lately quarries have increasingly tended to have stone crushing plants which manage to produce aggregates from natural stone waste. In particular, aggregates for the production of concrete (product code EN 12620) and aggregates for road and railway ballast (product code EN 13450:2003) can be produced from the recycling of this kind of stone waste. However, there are some crucial constraints for the re-use of dimension stone waste for the production of aggregates. Firstly, the market performance of aggregates mainly depends on the local demand for construction materials in the areas near the quarries where these materials are extracted and produced. Evidently, the economic value of aggregate resources, which is rather low, makes their importation not very profitable, because handling and transport costs must be added to the cost of the aggregates, resulting in a higher price. The importation of aggregates is also not really sustainable because of the environmental impact that the transport of materials may generate. Consequently, aggregates are mainly aimed at the local market, while dimension stones have a global market. Thus, if the building and construction market is experiencing weak or zero growth locally, quarrying companies are affected by the reduced demand for aggregates.

Additionally, comparing market prices for dimension stones with those for aggregates, the latter are much lower. In fact, due to the particular and delicate processing operations, higher prices for dimension stones may be expected. In contrast, aggregates can be produced without a difficult manufacturing process. For this precise reason, the dimension stone industry and the aggregate industry usually deal with different market sizes, potential, turnovers, and distribution processes. Even the most common units of measurement of dimension stone and aggregates are different. Equivalent square meters, as written above, for dimension stones, and cubic meters or tons for aggregates. However, it is possible to compare market prices for dimension stone exports and aggregates, both expressed in cubic meters. For instance, in 2008 Italy's processed stone exports amounted to 2686 USD per cubic meter, while the 2008 average reference price of aggregates in Europe was 15 USD per cubic meter, according to data reported by the European Environment Agency. Consequently, due to the lower economic value of aggregates with respect to ornamental stones, the re-use of dimension stone waste by producing aggregates might not be economically advantageous for quarrying companies. In fact, they still feel the need to seek new economically competitive by-products from quarry waste.

Before examining the second and third groups of waste taken into consideration, it is appropriate to briefly explain the phases of production of dimension stones and the related machinery, in order to understand better the different waste which is likely to be produced. Firstly, the extraction process involves cutting with diamond wire saws or chain saw cutting machines, drilling and bench tipping. These phases produce large amounts of dust and for this reason dust collectors are frequently used. Secondly, the sawing of huge raw pieces of dimension stone is usually carried out by means of a gang saw. In today's efficiency-aware quarrying plants, after adding water waste materials are collected below the machine, producing sludge. Then, it is flushed out through pipes. The slurry is eventually accumulated in the wastewater collection tank, at which point the recycling process starts. As a result, inert waste and water, which is put again in the quarry processing, are produced. Thirdly, after sawing, there is the processing phase, including sawing, polishing, cutting and the packaging operations. Polishing machines, edging and finishing machines, surface processing machines and all other equipment and products required for processing natural stones are included. As well as the sawing phase, the processing is characterized by the production of slurry.

The second group of waste taken into consideration is dust. Considerable amounts of dust and fine powders are produced in quarries as a result of the different production phases mentioned above. As waste, this dust may bring about harmful effects on human health such as asthma and lung cancer, owing to its very fine particle size. On the other hand, as a by-product, this powder proves to be very interesting, for it contains nearly the same elements as the original dimension stone. Consequently, the collection and re-use of dust waste is a matter of the utmost importance, both from the economic and the environmental health and protection points of view. Literature on this subject suggests the use of quarry dust in concrete mixtures, especially the use of marble and limestone dust in the field of self-compacting concrete applications (Felekoglu, 2007).

As noted above, the main phases of dimension stone quarrying are characterized by the extensive use of water, either as cooling agent for the machinery, or in order to remove dust and particles that can be generated in the production phases. This give rise to the last group of waste considered, the semi-slurry, slurry and cake. Slurry has variable composition, depending on both the original stone and the particular processing chosen. It includes water and dust obtained from the processing of the extracted materials. As already stated, nowadays the water is recycled and re-used onsite as cooling water and dust stabilizer in the extraction and the industrial processes. A drying process is carried out in order to remove possible harmful materials, such as sawdust and hydrocarbons. Thanks to press filters, up to 90% of the water can be recovered. Water and another material called sludge are obtained. The second usually has a high humidity content (22-28%) (OSNET, 2004). This sludge is frequently dumped or used in the necessary maintenance operations of the quarry. For instance, compact water-resistant layers are made from it in order to create quarry squares. Moreover, there are a number of studies dealing with the re-use of waste sludge, especially in the field of construction materials, such as concrete additives (Arslan et al., 2005; Corinaldesi et al., 2010) or bricks and other building elements (Marras et al., 2010; Bilgin et al., 2012; Galetakis et al., 2012), and so on.

### *1.4 Waste production trends: focus on China's and Italy's performance at the international level*

Usually, dimension stones are marketed and used in different countries from those in which they had been extracted, giving rise to an intense exchange at the international level. For this reason, the transportation cost has a significant role in the definition of market prices. In fact, frequently the price of exported stone products increases owing to transportation costs. As for commercial marbles or calcareous stones, which are the major product of the stone industry, extensive deposits are located all over the world, and especially in Italy, India, Pakistan, Spain, Greece, Brazil, China, Afghanistan, Turkey, Great Britain, and in the United States. Among these countries, China and Italy have been chosen for further investigation because China is the largest producer and Italy had been the world leader of the stone sector for centuries. Both therefore have a great influence on the market of natural stone. In addition, although China and Italy have each played a crucial role in the sector, they have different traditions and approaches.

Italy has been chosen to represent those Western countries that, despite currently facing an economic crisis, can still have great significance in the dimension stone sector. In contrast, while China is one of the most healthy economies in the world, the per capita consumption of dimension stone is still rather low with respect to that of Western countries, and Italy in particular. This means that in proportion Chinese people do not benefit from the exploitation of these natural resources as much as Italians do. Therefore, China has been selected from those Eastern countries that are becoming increasingly important in the worldwide economy in order to underline the differences between Eastern and Western approaches towards the development of the stone sector and its consequences on the environment. Also, by studying Italy's and China's production, their world interchange and their trend in time, it is possible to emphasize some risks and opportunities for the development of the sector.

In 2010 China confirmed its leading role in natural stone production, which accounts for half of total world production along with those of India and Turkey. Although Italy has experienced the general economic downturn which affected the whole sector from 2008, it still has high quarry production as well as a well-developed industry and high standards of quality and technology in the marble sector. From the above data, it can be seen that Italy ranked 5th in world production of dimension stone in 2010. Deposits of commercial marbles are located throughout the country, from the famous marble extracted from the Apuan Alps in Tuscany, to the internationally known travertine of Lazio and the more recent Marble District of Orosei on the island of Sardinia.

The previous paragraph gives an initial comparison between the production of China and Italy, and China's predominance in the dimension stone sector is clear. Further comparison from the perspective of import-export interchange between these countries and the rest of the world can be made. The effects on the production of waste are also outlined below.

Table 1.7 shows the stone interchange between China and the rest of the world for the period 2003-2010. From the data it can be seen that both raw production and the raw imports increased. It is possible to investigate the consequences from the perspective of the production of waste. Waste can be subdivided into quarrying waste and processing waste. Quarrying waste increases with the increase in raw production. Processing waste increases too, both for the same reason as for the quarrying waste and also because of an increase in imports. This means that increasing imports of raw materials to be processed have as a result higher amounts of processing waste. However, increasing amounts of imported raw material to be processed mean that for those amounts there is no quarrying waste, which is usually a huge percentage of the material extracted. Therefore, the importation of raw materials to be processed can be considered advantageous for a country's domestic production of waste. However, it should be pointed out that those quantities of raw materials had previously been extracted in another country. This could lead to some environmental risks. In fact, the importer country does not have to deal with the quarrying waste produced to extract the raw material, and also this country can export the processed product after it has gained an added value, that is at higher prices. On the contrary, the exporter country has to deal with an amount of quarrying waste whose original raw material is intended to be exported to another country at raw material prices, which are much lower than those of the processed material. Clearly, the exporter country has a modest economic revenue against a higher production of waste and potential environmental damage due to the accumulation of natural stone waste. China is an example of what has been happening in countries that are climbing into the top ten of dimension stone producers, such as India and Turkey.

**Table 1.7.** Stone Interchange China – Rest of World, years 2003 – 2010, thousand cubic meters (Montani, 2011).

| **year** | **Raw production** | **Raw Imports** | **Raw exports** | **Raw Availability** | ***IMPORTS*** | | | ***EXPORTS*** | | | **Balance of trade** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | ***Raw*** | ***Processed*** | **TOTAL** | ***Raw*** | ***Processed*** | **TOTAL** | |
| 2003 | 6,481 | 1,237 | 329 | 7,390 | 1,237 | 26 | 1,263 | 329 | 2,261 | 2,590 | 1,327 |
| 2004 | 6,667 | 1,534 | 498 | 7,703 | 1,534 | 20 | 1,554 | 498 | 2,292 | 2,790 | 1,236 |
| 2005 | 7,407 | 1,664 | 606 | 8,466 | 1,664 | 23 | 1,687 | 606 | 2,689 | 3,295 | 1,608 |
| 2006 | 8,333 | 2,184 | 387 | 10,130 | 2,184 | 41 | 2,225 | 387 | 3,441 | 3,829 | 1,604 |
| 2007 | 9,815 | 2,646 | 384 | 12,076 | 2,646 | 38 | 2,683 | 384 | 3,887 | 4,271 | 1,588 |
| 2008 | 10,185 | 3,012 | 290 | 12,908 | 3,012 | 27 | 3,040 | 290 | 4,078 | 4,368 | 1,328 |
| 2009 | 11,481 | 2,986 | 166 | 14,302 | 2,986 | 39 | 3,024 | 166 | 4,180 | 4,346 | 1,321 |
| 2010 | 12,222 | 4,541 | 247 | 16,516 | 4,541 | 19 | 4,560 | 247 | 4,381 | 4,628 | 68 |

In Table 1.8 the stone interchange between Italy and the rest of the world for the period of 2003-2010 is reported. While Italy's raw production was fairly steady over the period considered, raw imports along with processed exports decreased. Additionally, raw exports soared. These trends mean that Italy has increasingly chosen to manufacture few processed stone products in favor of the exportation of growing quantities of raw stone materials. As a consequence, for these exported amounts, there is quarrying waste but not processing waste. Therefore, Italy has been playing the role of the exporter countries aforementioned.

**Table 1.8.** Stone Interchange Italy – Rest of World, years 2003 – 2010, thousand cubic meters (Montani, 2011)

| **year** | **Raw production** | **Raw Imports** | **Raw exports** | **Raw Availability** | ***IMPORTS*** | | | ***EXPORTS*** | | | **Balance of trade** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | ***Raw*** | ***Processed*** | **TOTAL** | ***Raw*** | ***Processed*** | **TOTAL** | |
| 2003 | 2,907 | 748 | 320 | 3,336 | 748 | 93 | 841 | 320 | 818 | 1,137 | 296 |
| 2004 | 2,833 | 850 | 261 | 3,422 | 850 | 143 | 993 | 261 | 883 | 1,144 | 151 |
| 2005 | 2,778 | 747 | 367 | 3,158 | 747 | 173 | 920 | 367 | 789 | 1,156 | 237 |
| 2006 | 2,833 | 840 | 398 | 3,276 | 840 | 174 | 1,014 | 398 | 810 | 1,208 | 194 |
| 2007 | 2,870 | 821 | 433 | 3,259 | 821 | 163 | 983 | 433 | 805 | 1,238 | 254 |
| 2008 | 2,926 | 686 | 436 | 3,176 | 686 | 169 | 854 | 436 | 732 | 1,168 | 314 |
| 2009 | 2,778 | 439 | 458 | 2,759 | 439 | 151 | 590 | 458 | 592 | 1,050 | 460 |
| 2010 | 2,889 | 485 | 554 | 2,820 | 485 | 144 | 629 | 554 | 610 | 1,164 | 536 |

In conclusion, Western industrialized countries such as Italy, Spain and Portugal have to deal not only with huge amounts of waste accumulated over the past years, but also with increasing amounts of waste resulting from the current import-export policies in the world market for dimension stones. Western countries may be adversely affected by these policies from an environmental-awareness point of view, even though they have a long tradition of quarrying, which had given them time to search for and improve their environmental safeguarding policies, production efficiency and re-use of stone waste. For this reason, dealing with natural stone waste is a critical issue, which not only affects developing countries in which environmental awareness is not widespread, but also industrialized countries.

### *1.5 Dealing with natural stone waste: risks and opportunities*

From Table 1.3 it can be deduced that dimension stone has an average efficiency (i.e. the ratio between the total volume extracted and total raw dimension stones selected for the market) of about 70%. Natural stone waste could either be stored in dumps or re-used according to the various applications described above. Generally, after extraction and industrial processing, this waste is preferably dumped inside the quarry boundaries or in places as close as possible to the quarry. As a consequence, quarrying companies all over the world are dealing with larger and larger amounts of stone waste and are constantly seeking new possibilities to re-use it as economically competitive by-products.

A review of opportunities and risks related to the choice between storing in dumps or re-using dimension stone waste is presented below. In fact, inadequate management of this waste can lead to economic, environmental and health problems.

- *Economic problems*

From the economic perspective, quarrying companies have to manage more than a half of the gross production of dimension stone which actually is waste. As the volume of waste increases, both productivity and revenues decrease. This is the first reason why quarry operators try to minimize the amount of waste produced. If this waste is accumulated in landfills, they could be either inside or outside the quarry. Waste disposal inside the quarry generates problems such as less space to use for excavation operations, and risks to the health and safety of quarry workers. They are indeed more exposed to airborne dust from uncompacted waste and to the risk of falling rocks from unconsolidated faces in superficial deposits. Conversely, if waste is stored in landfills outside the quarry, operators have to accept additional costs for transportation and landfill charges. In addition, stricter policies penalize quarrying companies in Western Countries from the economic perspective. In fact, in these countries there is tougher environmental legislation, more complicated requirements to obtain permission for mining and quarrying, and a more complex system of landfill charges than in Eastern or developing countries, which have less stringent regulation.

It is also important to point out that great quantities of dumped waste occupy portions of the territory which cannot be used for other purposes, such as agricultural or residential development. These land uses are productive and increase the value of the land, which is not the case in land used for landfill sites. This is a loss that the whole society has to bear.

- *Environmental problems*

From the environmental perspective, huge deposits of dimension stone waste in landfills lead first of all to a gradual deterioration and poor perception of the landscape resulting in a negative visual impact. Secondly, potentially harmful impacts can emerge as well. Disposal of stone waste in a landfill gives rise to such issues as slope erosion, landslides, and the risk of serious environmental degradation of the areas. Fine particles of stone waste can be carried by the wind to nearby areas and deposited on the vegetation. This could affect agriculture and also bring about topographic changes at the local level. Moreover, if stone slurry is not managed properly, it can infiltrate into the ground or in waterways and cause hazardous pollution.

Additionally, large quantities of stone waste can be considered an unused potential resource. On the contrary, if its re-use were fostered, it could be used in place of natural materials. In this way, there would be fewer new quarries or less intensive production of raw stone.

- *Health problems*

Increasing accumulation of natural stone waste in dumps might lead to health problems for employees and local communities living in the area. It frequently occurs that, even though the original stone is not a harmful material by its very nature, huge amounts of stone waste can become hazardous. As solid, this waste should be consolidated in slopes with stabilization processes so as not to cause injuries to employees. Also, it can be wind-borne, bringing about respiratory problems, and ocular or dermal irritation for both employees and the residents of nearby areas. As liquid, natural stone slurry can leak into waterways and affect the availability of safe drinking water in the area.

After having discussed the three typologies of problems caused by incorrect management of natural stone waste, let us take into consideration the possible solutions that quarrying companies might find. In Figure 1.3 the quarrying and processing phases are briefly reported, along with the kind of waste stream produced, in order to compare three different strategies for natural stone waste management.

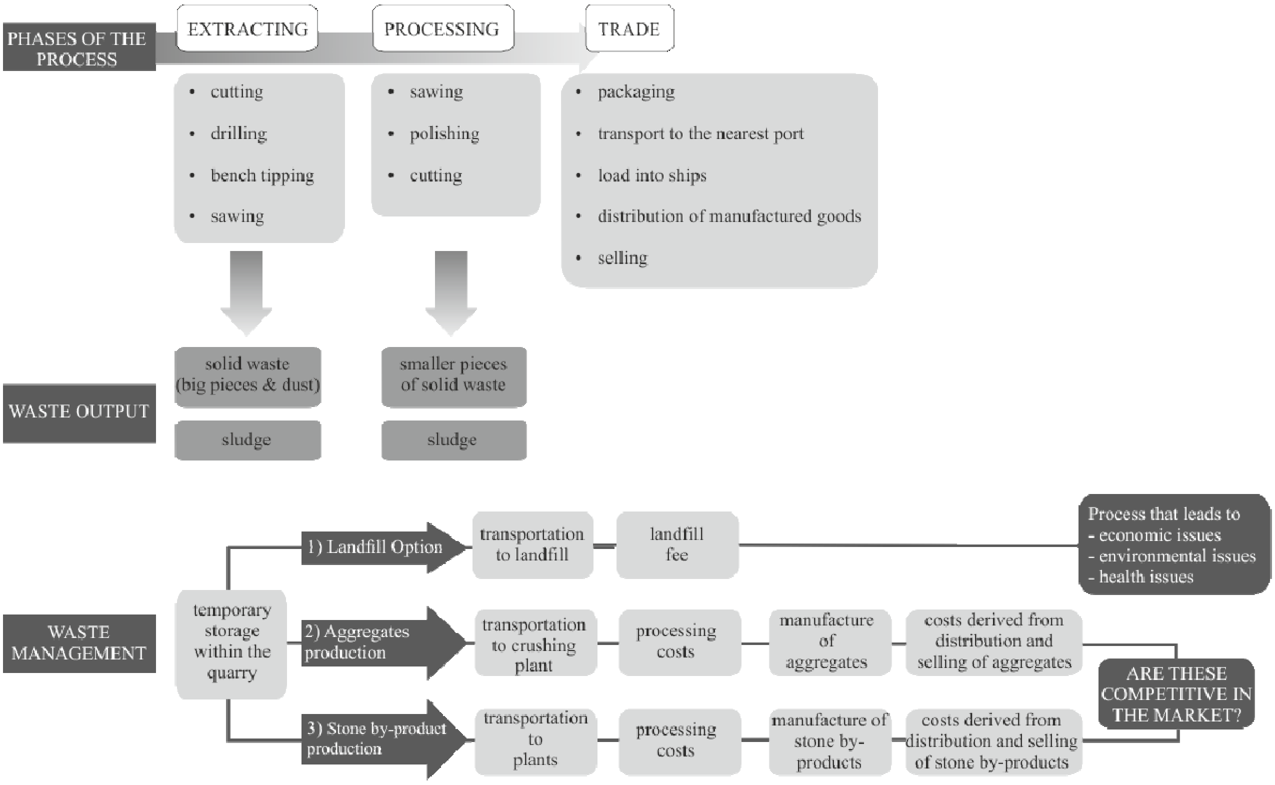

**Figure 1.3.** Quarrying and processing phases, corresponding waste streams and three different waste management operations.

The first option is waste disposal in landfills. This seems not only to be very costly, but it also leads to a worse situation from the economic, environmental and health points of view. The last two are mainly perceived by local communities and governments, whilst stone producers are mainly concerned about the economic loss. In fact, it turns out that with the landfill option, they have to accept transportation costs and landfill charges while receiving nothing in return. In fact, local communities and governments are also affected by the economic factor because dealing with environmental deterioration and the associated health hazards requires investment. Furthermore, it frequently occurs that legislative measures oblige quarrying companies to pay compensation for the environmental pollution they cause. Therefore, stone producers are also concerned about the environmental and health aspects.

The second option is the production of aggregates from natural stone waste. Quarrying companies have to bear the transportation cost to the crushing plants, or if it is located within the quarry, it is a further process phase which has to be managed. Also, they have to bear the costs of processing operations and from the distribution and sale of aggregates. This could be a good solution from the environmental and health point of view, because the accumulation in temporary sites is for a very short time and the disposal in landfill is avoided. However, as already mentioned, the market for aggregates is very different from that of dimension stones. Indeed, it is hard for quarrying companies that normally operate in the dimension stone market to deal with aggregates. In fact, the latter market is much smaller, the distribution is local instead of international, and the prices of aggregates are significantly lower than those of dimension stones. For this reason, while many companies have the potential to start up the production of aggregates from their natural stone waste, most choose not to do so owing to the fact that either it is not profitable or the demand of the local market has already been satisfied.

The third option presents phases very similar to the second. The difference is that instead of aggregates, quarrying companies should start the production of high-quality by-products from natural stone waste. These might be materials such as precast products of various type for building activity, since there is a direct correlation between construction activities and the demand for stone products. In this case, the market for these by-products would be international, and prices would be higher than those of both aggregates and dimension stones. As a result, the distribution and sale phases should follow the same rules as those of dimension stones, and they would also be at international level. To sum up, even though quarrying companies would initially have to invest in manufacturing new stone by-products, they would profit from the added value of these products. In fact, the revenue gained by selling them would be considerably higher than that gained by selling lower-price products such as aggregates.

## *References*

H. Akbulut and C. Gürer (2007). Use of aggregates produced from marble quarry waste in asphalt pavements, Building and Environment 42, 1921-1930.

N. Almeida, F. Branco, and J.R. Santos (2007). Recycling of stone slurry in industrial activities: Application to concrete mixture, Building and Environment, 42, 810-819.

E. I. Arslan, S. Aslan, U. Ipek, S. Altun, and S. Yazicioglu (2005). Physico-chemical treatment of marble processing wastewater and the recycling of its sludge, Waste Management & Research 23, 550-559.

Aukour F. J., Al-Qinna M. I. (2008). Marble Production and Environmental Constrains: Case Study from Zarqa Governorate, Jordan, Jordan Journal of Earth and Environmental Sciences 1(1), 11-21.

N. Bilgin, H.A. Yeprem, S. Arslan, A. Bilgin, E. Günay and M. Marsoglu (2012). Use of waste marble powder in brick industry, Construction and Building Materials 29, 449–457.

V. Corinaldesi, G. Moriconi, T.R. Naik (2010). Characterization of marble powder for its use in mortar and concrete, Construction and Building Materials 24, 113–117.

C. Coroneos, P. Hisinger and R.J. Gilkes (1996). Granite powder as a source of potassium for plants: a glasshouse bioassay comparing two pasture species, Fertilizer Research 45, 143–152.

Decision 94/3/EC: Commission Decision of 20 December 1993 establishing a list of wastes pursuant to Article 1a of Council Directive 75/442/EEC on waste - European Waste Catalogue (EWC).

Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives (Text with EEA relevance).

T.P. Dolley (2000). “Stone, Dimension. US Geological Survey Minerals Yearbook”, Reston, Virginia.

European Aggregates Association [UEPG] (2009). “Annual review 2008-2009”, UEPG aisbl, Brussels.

B. Felekoglu (2007). Utilisation of high volumes of limestone quarry wastes in concrete industry (self-compacting concrete case), Resources, Conservation and Recycling 51, 770–791.

M. Galetakis, G. Alevizos and K. Leventakis, (2012). Evaluation of fine limestone quarry by-products, for the production of building elements – An experimental approach, Construction and Building Materials 26, 122–130.

O. Gencela, C. Ozelb, F. Koksalc, E. Erdogmusd, G. Martínez-Barrera and W. Brostowf (2012). Properties of concrete paving blocks made with waste marble, Journal of Cleaner Production 21, 62-70.

M. N. Hassan (2000). Policies to improve solid waste management in developing countries: some insights in Southeast Asian Countries. In: Proceedings of the 2nd International Conference on Solid Waste Management, eds. E.E. Chang, P.C. Chiang, C.P. Huang and N.C. Vasuki, p. 191-207. Taipei, Taiwan: Environmental Protection Administration, Republic of China.

H. Hebhoub, H. Aoun, M. Belachia, H. Houari and E. Ghorbel (2011). Use of waste marble aggregates in concrete, Construction and Building Materials 25, 1167–1171.

Z. Karaca, A. Pekin and A. H. Deliormanl (2012). Classification of dimension stone wastes, Environmental Science and Pollution Research 19, 2354–2362.

F. Loukil and L. Rouachedb (2012). Modeling packaging waste policy instruments and recycling in the MENA region, Resources, Conservation and Recycling 69, 141– 152.

G. Marras, N. Careddu, C. Internicola, and G. Siotto (2010). Recovery and reuse of marble powder by-product, Proc. Global Stone Congress, Alicante, ESP, 2010.

R. R. Menezes, H. S. Ferreira, G. A. Neves, H. de L. Lira and H. C. Ferreira (2005). Use of granite sawing wastes in the production of ceramic bricks and tiles, Journal of the European Ceramic Society 25, 1149–1158.

C. Montani (2011). “XXII Report 2011 world marble and stones”, Aldus Casa di Edizioni, Carrara.

Organization for Economic Co-operation and Development [OECD] and International Energy Agency [IEA] (2008). “World energy outlook 2008”, IEA Publications, Paris - available at: http://www.worldenergyoutlook.org.

OSNET Editions vol. 9 (2004). “Complementary technologies for stone processing”, edited by S. Midha and I. Paspaliaris, Athens.

S.R. Parthan, M. W. Milke, D. C. Wilson, and J. H. Cocks (2012). Cost estimation for solid waste management in industrialising regions – Precedents, problems and prospects, Waste Management 32, 584–594.

Resource Conservation and Recovery Act, P.L. 94-580, 90 Stat. 2795, 42 U.S.C. § 6901 et seq., October 21, 1976.

D. Rockliff (1996). Low-grade quarry products, reclaimed aggregates and inert wastes - Their use in unbound mixtures for road pavements, Waste Management 16, 83-85.

Sardegna Ricerche and Consorzio 21 (2002). “Natural Stone from Sardinia. Technical Handbook”, Sardegna Ricerche, Cagliari.

A.M. Segadaes, M.A. Carvalho and W. Acchar (2005). Using marble and granite rejects to enhance the processing of clay products, Applied Clay Science 30, 42– 52.

B. Silva, R. Paradelo, N. Vázquez, E. García-Rodeja and M. Barral, (2012). Effect of the addition of granitic powder to an acidic soil from Galicia (NW Spain) in comparison with lime, Environmental Earth Sciences, available at: http://link.springer.com/, http://dx.doi.org/10.1007/s12665-012-1747-3.

D. V. Smith, K. F. Jalal, and Asian Development Bank [ADB] (2000). “Sustainable development in Asia”, Asian Development Bank.

The World Bank (1999). “Urban Development Sector Unit East Asia and Pacific Region, What a Waste: Solid Waste Management in Asia”, Washington DC: World Bank.

J. T. Tukahirwa, A. P. J. Mol, and Oosterveer P. (2013). Comparing urban sanitation and solid waste management in East African metropolises: The role of civil society organizations, Cities 30, 204–211.

United Nations Environment Programme's [UNEP] (1999). “Global Environment Outlook (GEO) 2000”, UNEP Nairobi.

US Department of the Interior, United States Geological Survey [USGS] (2011). “Mineral Commodity-Summaries 2011”. Reston, Virginia, ISBN 978-1-4113-3083-2.

United Nations Commodity Trade Statistics Database, available at: http://comtrade.un.org/db/default.aspx.

C.M.F. Vieira, T.M. Soares, R. Sánchez and S.N. Monteiro (2004). Incorporation of granite waste in red ceramics, Materials Science and Engineering A 373, 115–121.

VV. AA. (2002). “Guida all’industria estrattiva e al riciclaggio”, quarta ed, (Guide to the mining industry and to recycling, fourth edition) - supplement to Quarry and Construction 10, Parma, IT: Edizioni Pei.

D. C. Wilson, C. Velis, and C. Cheeseman (2006). Role of informal sector recycling in waste management in developing countries, Habitat International 30, 797–808.

# Chapter 2. The geographical setting of the study area

## *2.1 Orosei Marble District*

The study presented in this dissertation was conducted in the Sardinia region (Italy). The Sardinia region is characterized by great geological variability. A large number of sedimentary, volcanic, metamorphic and intrusive rocks, dating back to different geological cycles from Prepaleozoic to Quaternary, are found on this island (Marini et al., 2006, Region of Sardinia, 2007).

This work considers natural stone waste from the industrial quarry district located in the Gulf of Orosei (North East Sardinia, Figure 2.1). It is an area rich of calcareous deposits, mainly formed by limestones, dolomitic limestones and dolostones. In particular, the Sardinian territory is divided into eight geographic areas featuring several quarries producing stones with homogeneous lithotypes. These areas correspond to eight so-called “Quarrying Basins”, in which the Orosei Basin, producing limestone called “Orosei Marble” is encompassed.

**Figure 2.1.** Location of the Orosei Marble District, N-E Sardinia (IT).

Even though over the past decade Sardinian production of dimension stone has dropped in line with the contraction in all of Italy as a consequence of the global crisis, it is noticeable that this phenomenon has principally concerned the granite sector. Table 2.1, 2.2 and 2.3 (Region of Sardinia, 2007; USGS, 2009; USGS, 2011) report and compare data on the Italian and Sardinian production of main dimension stones, which are actually commercial marbles and granites. From these data it is noticeable that the granite sector has reported a decrease in production from 322,000 cubic meters/year to 170,423 cubic meters/year (-47%). In contrast, Orosei Marble has shown a substantial balance. Furthermore, whereas in Italy the percentage subdivision between marble and granite production remains approximately the same (75-80% and 25-20% respectively), in Sardinia the production of Orosei Marble has increased from 21% to 33%.

**Table 2.1.** Production of main Dimension Stones, Italy and Sardinia [cubic metres].

| | 2001 | | 2004 | | 2006 | |
|---|---|---|---|---|---|---|
| | **Italy** | **Sardinia** | **Italy** | **Sardinia** | **Italy** | **Sardinia** |
| **Calcareous stone (*)** | 2,552,500 | 85,000 | 2,833,846 | 76,311 | 2,645,769 | 85,468 |
| **Granite** | 735,962 | 322,000 | 1,014,231 | 153,082 | 728,462 | 170,423 |
| **Total** | 3,288,462 | 407,000 | 3,848,077 | 229,393 | 3,374,231 | 255,891 |

**Table 2.2.** Percent subdivision of Italian and Sardinian production of main dimension stones.

| | 2001 | | 2004 | | 2006 | |
|---|---|---|---|---|---|---|
| | **Italy** | **Sardinia** | **Italy** | **Sardinia** | **Italy** | **Sardinia** |
| **Calcareous stone (*)** | 78 | 21 | 74 | 33 | 78 | 33 |
| **Granite** | 22 | 79 | 26 | 67 | 22 | 67 |
| **Total** | 100 | 100 | 100 | 100 | 100 | 100 |

**Table 2.3.** Sardinia percent of Italian total production of main dimension stones.

| | 2001 | | 2004 | | 2006 | |
|---|---|---|---|---|---|---|
| | **Italy** | **Sardinia** | **Italy** | **Sardinia** | **Italy** | **Sardinia** |
| **Calcareous stone (*)** | 100 | 3 | 100 | 3 | 100 | 3 |
| Granite | 100 | 44 | 100 | 15 | 100 | 23 |

*(*) Regarding Italian data, calcareous stone encompasses Dolomite and Marble and travertine, crude. As for the Sardinian data, calcareous stone only encompasses Orosei Marble, because it is the major calcareous product from the Sardinian extractive industry.*

The area in which Orosei Marble is extracted is classified both at national and regional level as one of the Sardinian dimension stone districts, which produce stone with homogeneous petrographic characteristics (Italian National Law no. 317, 1991); the other four produce granite. Currently, fourteen active quarries operate in this district and other sixteen are inactive, although these figures could vary from year to year depending upon economic conditions (Sardegna Ricerche, 2002; Region of Sardinia, 2007).

## *2.2 Materials: Orosei Marble*

The Marble of Orosei is the most important stone of Sardinia in the production of limestone. Although the commercial term is “marble”, this type of stone has a sedimentary origin, and more specifically is Mesozoic limestone and dolomite dating from the Jurassic and the Cretaceous periods even though of a non-metamorphic origin (Marcello *et al.* 2008).

Orosei Marble entails several commercial types, called Clear-coloured Marble (available varieties: Fiocco di neve - “sprinkled” snow; Perlato - Pearly; Nuvolato - Cloudy) and Medium-veined Marble, featuring several different colours and veining, shown in Figure 2.2.

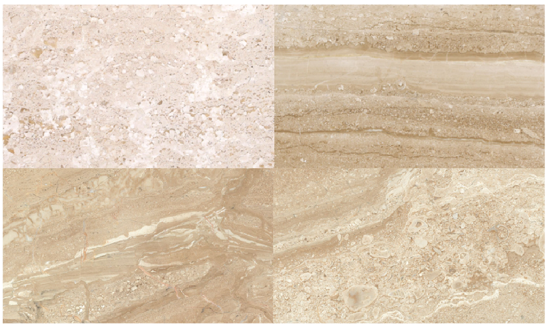

**Figure 2.2.** Four different varieties of Orosei Marble.

This material has good physical and mechanical properties. Table 2.4 compares mean values of the average of the different varieties of Orosei Marble aforementioned (made available by the quarrying companies of the Orosei Marble District) with the mean values of the same properties recorded for similar types of marble from Tuscany, the Apuan marbles (average values of two different varieties, White and Veined Marble) (Region of Tuscany, 1992; Sardegna Ricerche, 2002), which have an ancient historical background and are known all over the world as stones of excellent quality.

**Table 2.4.** Comparison of Physical and Mechanical Characteristics of Orosei and Apuan Marbles (mean values).

| | units | **APUAN MARBLES** | **OROSEI MARBLES** |
|---|---|---|---|
| Breaking load (under uni-axial compression) | | | |
| *on dry test piece* | kg/cm$^2$ | 1,309 | 1,679±271 |
| *after freeze/thaw cycles* | | 1,260 | 1,527±285 |
| Flexural strength | kg/cm$^2$ | | |
| *- on dry test piece* | | 184 | 150±39 |
| Impact resistance (height of fall) | | | |
| *30 mm thick test piece* | cm | --- | 30 |
| *50 mm thick test piece* | | 55.61 | --- |
| Frictional wear | mm | 5.54 | 4.11±0.65 |
| Linear elasticity modulus (static) | kg/cm$^2$ | 677,889 | 778,254±77,930 |
| Imbibition coefficient | ‰ | 1.40 | 5.13±2.47 |
| Weight per unit volume | kg/m$^3$ | 2,691 | 2,685±41 |

From this data set some positive features of Orosei Marble can be pointed out. Firstly, its mean breaking load resistance is higher than that of Tuscan marbles. In contrast, flexural strength is lower, but still meets legislative requirements. Regarding impact resistance, a direct comparison is impossible due to the fact that available information is only related to commercial samples, whose thickness is different for Orosei and Apuan Marble (30 mm and 50 mm respectively). However, it is possible to say that Orosei Marble has good and probably higher impact resistance because of the different thicknesses. In addition, from the frictional wear data, Orosei Marble happens to be more resistant to sand abrasion. It also shows a higher modulus of linear elasticity deriving from its compactness. In conclusion, although the mean value of the imbibition coefficient is higher for Sardinian Marble, it is still frost-proof, as a result of uniaxial compression and flexural strength tests undertaken after 20 freeze/thaw cycles.

## *2.3 Natural Stone Waste in Sardinia*

Generally, after all the industrial processing, natural stone waste is preferably dumped inside the quarry boundaries or in places as close as possible to the quarry. Quarrying companies are dealing with larger and larger amounts of this waste and are constantly seeking new possibilities to re-use them as economically competitive by-products. As stated above, the main dimension stone products in Sardinia are granite and Orosei Marble. In Table 2.5 their waste production is analyzed. From these data it can be seen that granite has a medium efficiency (i.e. the ratio between the total volume extracted and total raw dimension stones selected for the market) of 60%, whereas Orosei Marble efficiency is slightly lower at 50% (Region of Sardinia, 2006). Thus, in Sardinia there is an annual average production of about 600,000 cubic meters of natural stone waste, from which more than 265,000 cubic meters/year are re-used, mainly for the production of civil and industrial aggregates. The remaining part is stored in dumps, in which about 11,500,000 cubic meters of natural stone waste have already been collected.

**Table 2.5.** Natural stone waste and dumps in dimension stone quarries of Sardinia (**).

| | | **Granite** | **Orosei Marble** | **Other stones** | **TOTAL** |
|---|---|---|---|---|---|
| **Active Industrial Units** | *Number* | 64 | 11 | 12 | 87 |
| | *Average quarry efficiency (total volume extracted/total raw dimension stones selected)* | 0.6 | 0.5 | 0.6 | 0.57 |
| | *Natural stone waste [cubic meters]* | 323,546 | 265,321 | 5,551 | 594,418 |
| | *Total volume dumped [cubic meters]* | 6,981,310 | 787,000 | 84,750 | **7,853,060** |
| | *Current alternative reuse of natural stone waste [cubic meters]* | | | | |
| | *- shapeless blocks* | 10,100 | 0 | 0 | 10,100 |
| | *- civil and industrial aggregates* | 184,914 | 67,858 | 325 | 253,097 |
| | *- stone filling for ports* | 3,030 | 0 | 0 | 3,030 |
| **Inactive Industrial Units** | *Number* | 65 | 5 | 12 | 82 |
| | *Estimated total volume dumped [cubic meters]* | 3,334,466 | 124,000 | 184,800 | **3,643,266** |

*(**)Currently, regarding the two dimension stones considered, i.e. Granite and Orosei Marble, there are available data only on the total Sardinian production. In fact, data on the production of the case studied are not public yet. However, they are included in these data and their collection is the next step of this research.*

Special attention is focused on natural stone waste from Orosei Marble. Indeed, there is a significant difference between waste from Orosei Marble and from granite: the former is quantified as about 800,000 cubic meters, while the latter is almost 7,000,000 cubic meters. The reason is twofold: first, calcareous stones are not too costly to process, and their properties are still good for their use in producing aggregates. Secondly, the Orosei Marble district is characterized by the particular proximity of the quarries, which established a consortium that manages and shares the same dump. In contrast, dealing with natural stone waste from Sardinian granite quarries is a crucial issue, not least because this industry has been operating for very many years, resulting in huge amounts of quarry waste. Moreover, while granite is also an excellent material, each quarry has its own dump in which waste is stored either neatly or not.

### 2.4 The selection of marble waste

The next step of this study involved the localization of some quarries where Orosei Marble is extracted and the preliminary contacts with quarrying companies potentially interested in the research. In the selection of these companies, great importance was attached to their being economically viable businesses despite the widespread crisis of this industry. In addition, they show particular concern for environmental sustainability and great interest in the search for a standardized methodology to re-use natural stone waste. They also manage to produce and guarantee constant waste streams, which is a prerequisite for assuming a leading role in the market of products derived from the recovery of quarry waste.

The stone waste object of this study was supplied by a quarrying company called S.I.M.G. s.r.l. Data on the quarry chosen as case study are reported in Table 2.6, and its aerial view is reported in Figure 2.3 and a panoramic view in Figure 2.4.

**Table 2.6.** Data on the Case Study located in the Orosei Marble District (Region of Sardinia, 2007).

| | Municipality | Quarry name | Beginning of the activity (year) | Trade name | Material | Reserves (years) | Quarry extent [Ha] |
|---|---|---|---|---|---|---|---|
| **Case Study** | Orosei | Canale Longu | 1972 | Orosei Marble | Limestone | 50 | 4,796 |

**Figure 2.3.** Aerial view of the quarry "Canale Longu" located in the Orosei Marble District.

**Figure 2.4.** Panoramic view of the quarry "Canale Longu" located in the Orosei Marble District.

## *References*

Legge 5 ottobre 1991, n. 317. Interventi per l'innovazione e lo sviluppo delle piccole imprese » *[Italian Act October 5, 1991, no. 317: Interventions for the innovation and the development of small enterprises]*.

C. Marini, S.Naitza and S.Tocco (2006). The granite district of Buddusò -Alà dei Sardi (Sardinia): geopetrographic aspects, environmental impact of quarrying activity and hypotheses for the recovery and the exploitation of inactive quarries (Il distretto del granito di Buddusò -Alà dei Sardi (Sardegna): aspetti geopetrografici, impatto ambientale dell' attività di cava e ipotesi per il recupero e la valorizzazione dei siti estrattivi dismessi), Proc. Stone resources from Ancient times to Today in the Mediterranean Region (Le Risorse Lapidee dall'antichità ad Oggi in Area Mediterranea) Conf., Torino, IT, 2006.

Region of Tuscany - ERTAG (1992). "Apuan Marbles", Firenze, IT: Industria italiana del Marmo.

Region of Sardinia (2006). "2004 Sardinia Regional Census of mining activities (quarries and mines)", Cagliari, IT.

Region of Sardinia (2007). "Sardinian Regional Plan for mining and quarrying activity", Cagliari, IT.

Sardegna Ricerche and Consorzio 21 (2002). "Natural Stone from Sardinia. Technical Handbook", Sardegna Ricerche, Cagliari.

United States Geological Survey [USGS] (2009). "2006 Minerals Yearbook Italy", Reston, VA.

United States Geological Survey [USGS] (2011). "2009 Minerals Yearbook Italy", Reston, VA.

# Chapter 3. Characterization of the Stone Waste Materials

At the beginning of the experimental work, some quarrying companies potentially interested in the research were contacted and asked to provide their stone waste. It was finally supplied by an enterprise which is member of the Orosei Marble District.

A physical, a chemical, and a mineralogical characterization were performed in order to highlight the specific properties of the waste material so as to allow for its use for commercial purposes. Additionally, it was investigated the potential harmfulness of the waste collected and verified its compliance with current legislation on hazardous and pollutant elements.

Three different typologies of waste were considered (Figures 3.1 and 3.2):

1) rejected stone fragments and trimmings, henceforth named CC;

2) dust and fine powder, henceforth named CSG;

3) slurry from the filter press, which is mud made of powder and water; henceforth named CFP.

**Figure 3.1.** From the left: rejected stone fragments and trimmings (CC); dust and fine powder (CSG); slurry from the filter press (CFP).

**Figure 3.2.** Plastic bags of each of the waste typologies considered.

Each typology was directly collected from the production plant; in particular, samples of CFP were taken from the filter press exit, whilst the remainder of the waste was collected from the temporary storage sites inside the quarry.

The following analyses were conducted on each typology of waste:

I. Grain size distribution;
II. Chemical analysis and LOI (Loss On Ignition);
III. Leaching test and concentration of minor elements;
IV. Density measurement;
V. Moisture content;
VI. Mineralogical analysis (X-ray diffraction measurement).

Before starting the analyses, the materials were prepared in order to obtain representative samples for the three typologies of waste. Firstly, the total sample was placed into an oven so as to dry it. Afterwards, the total sample was reduced to a size that could be tested, meaning that the sample should be representative of the material in the stockpile. This procedure is commonly known as quartering, by means of which the waste materials were split into the proper test sample.

### *3.1 Grain size distribution*

The particle diameters of the samples were determined through the grain size analyses. In Figures 3.3 and 3.4 the grain size information for CSG and CFP represented in logarithmic scale are reported. The graphs show the cumulative weight percentage by particle size of the sample. In other words, the fraction that is finer than each subsequent grain size is shown. As far as CSG is concerned, the main fraction of the material is included between 0.125 and 2 mm, thus in the range of sand, whilst about 80% of particles have the diameter smaller than 200 mm.

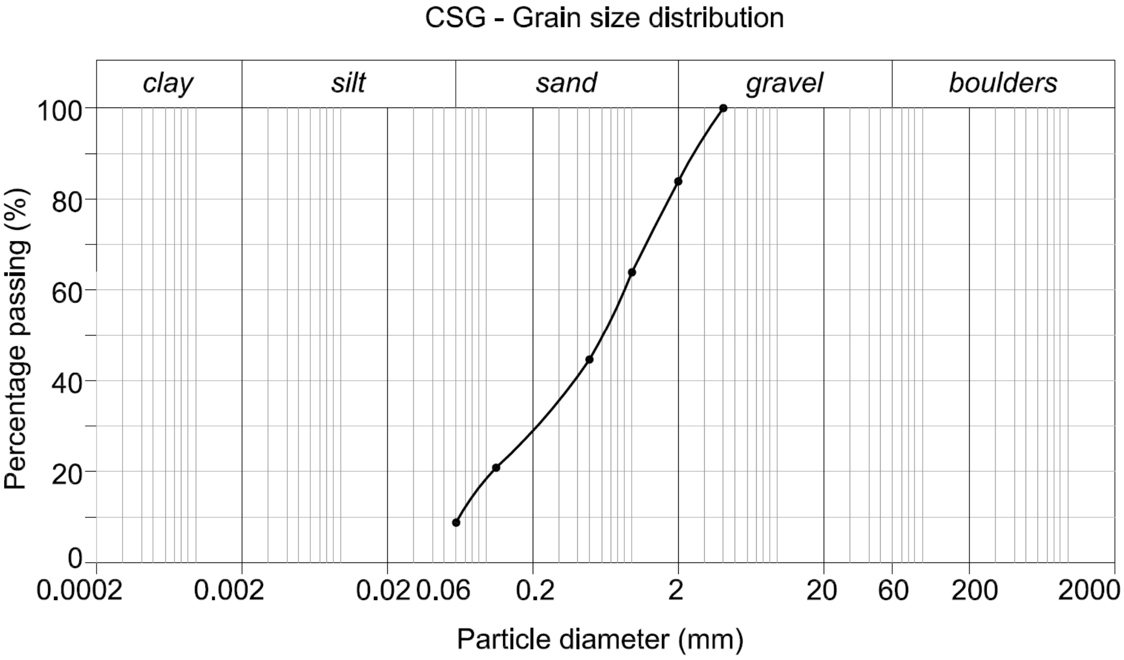

**Figure 3.3.** Grain size distribution of CSG.

Concerning CFP, its pattern has extremely fine particles, with the main fraction of the material under 25 mm, thus in the range of silt.

Since the sample named CC is made of stone fragments and trimmings of different sizes and shapes, its grain size is meaningless. It was crushed afterwards according to the grain size distribution needed in order to produce by-products object of this dissertation.

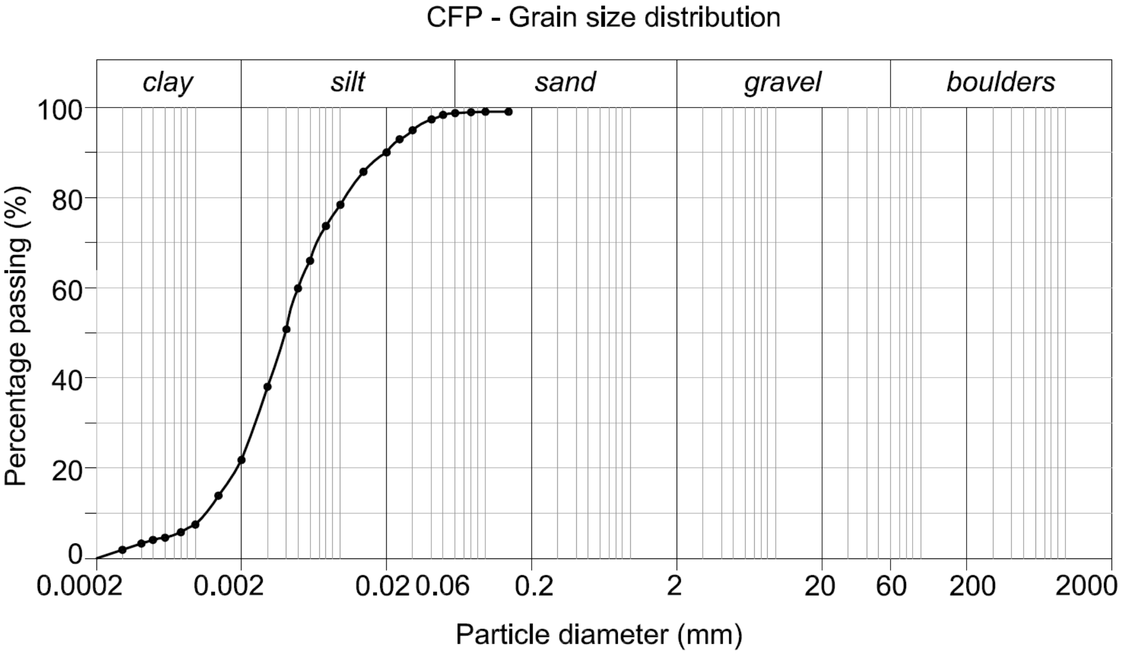

**Figure 3.4.** Grain size distribution of CFP.

### 3.2 Chemical analysis and LOI (Loss On Ignition)

The chemical composition of the materials studied permitted to understand the characteristics of the materials, which are of the utmost importance in order to define their most correct use.

The procedure allowed samples, mixed with lithium tetraborate, to be fused in a muffle furnace. After completing the fusion, and the crucibles having cooling down, the samples were placed in a beaker in a nitric acid solution (Boar, 1970). Major elements were therefore determined through Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and expressed as a percentage by mass of the quartered and dried samples. Since the materials are made of stone waste, their composition is expressed in terms of Aluminum, Iron, Manganese, Magnesium, Potassium, Sodium, Titanium, Phosphorus, Silicon, and Calcium Oxides. To these parameters it is added the percentage of Loss On Ignition (LOI), evaluated from the thermal mass loss which undergoes a sample of material at 950°C until a constant value is reached.

According to the data reported in Table 3.1, these materials have high content of CaO, as a result of their provenance from calcareous stone.

**Table 3.1.** Chemical analysis and Loss On Ignition conducted on the selected fractions of Orosei Marble waste.

| Analyte | CSG – dust and fine powder [%] | CFP – slurry from filter press [%] | CC – rejected stone fragments and trimmings [%] |
|---|---|---|---|
| $Al_2O_3$ | 0.020 | 0.043 | 0.044 |
| $Fe_2O_3$ | 0.021 | 0.028 | 0.054 |
| MnO | 0.003 | 0.007 | 0.006 |
| MgO | 0.472 | 0.394 | 0.485 |
| $K_2O$ | 0.023 | 0.042 | 0.014 |
| $Na_2O$ | 0.035 | 0.053 | 0.050 |
| $TiO_2$ | 0.001 | 0.003 | 0.002 |
| $P_2O_5$ | 0.014 | 0.010 | 0.048 |
| $SiO_2$ | 3.386 | 3.455 | 0.250 |
| CaO | 51.650 | 49.830 | 54.720 |
| LOI | 43.650 | 44.550 | 43.960 |
| Total | 99.275 | 98.415 | 99.633 |

### 3.3 Leaching test and concentration of minor elements

A leaching test was undertaken in compliance with UNI EN 12457-2 in order that the possible presence of hazardous elements in the stone waste could be detected. In fact, since each typology of waste considered is the result of quarrying and industrial processing, their containing negligible amounts of impurities and pollutants was to be proven. Also, their compliance to current Italian waste legislation was investigated. Chlorides and sulphates were determined in agreement with the Italian standard test procedure (UNI 8520) and subsequent analyses were carried out through ion chromatography.

As it can be noticed from Table 3.2, all parameters are below the legislation limits, therefore it will be hypothetically possible for this waste to undergo the simplified procedures for recovery and re-use introduced by the Italian Decree 152/2006.

**Table 3.2.** Comparison between the Legislation limits and the results of the leaching test conducted on the selected fractions of Orosei Marble waste.

| PARAMETER | LEGISLATION LIMIT [mg/l] Italian Decree 186/2006 | CSG [mg/l] | CFP [mg/l] | CC [mg/l] |
|---|---|---|---|---|
| **Fluoride** | 1.5 | 0.1301 | 0.0375 | 0.5144 |
| **Chlorides** | 100 | 1.1530 | 5.1357 | 0.9578 |
| **$N\text{-}NO_2$** | - | 0 | 0.5007 | 0 |
| **$N\text{-}NO_3$** | 50 | 0.0155 | 0.1150 | 0 |
| **$SO_4$** | 250 | 2.8245 | 20.2422 | 3.0712 |
| **pH** | 5.5 < > | 9.85 | 9.30 | 10.78 |

Additionally, trace elements (those elements in the samples having an average concentration of less than 0.1%) were also determined. The procedure consisted in digesting 1 g of material with a concentrated acid mix ($HNO_3$/HCl/HF). After that, the residue was diluted in a solution of distilled water and $HNO_3$ (1%). The results are reported in Table 3.3 and expressed as part per million (ppm or mg/l). Minor metals concentrations in filtered eluates and after the acid digestion and alkaline fusion were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

As it is possible to understand from Tables 3.2 and 3.3, all concentrations are below the legislation limits and they are also below the concentration limits for waste acceptability in landfills (Italian Decree Sept. 2010). Thus, the materials analysed can be considered as non-hazardous waste and re-used as secondary raw materials, which is the purpose of this dissertation.

**Table 3.3.** Concentration of minor elements in the selected fractions of Orosei Marble waste.

| Analyte | Detection limit [mg/l] | CSG [mg/l] | CFP [mg/l] | CC [mg/l] | LEGISLATION LIMIT *Italian Decree 186/2006 (simplified procedures for recovery)* | LEGISLATION LIMIT *Italian Decree Sept. 2010 L/S=10 1/kg (concentration limits for waste acceptability in landfills) [mg/l]* |
|---|---|---|---|---|---|---|
| **Ba** | 0.0001 | 0.007 | 0.007 | 0.778 | 1 mg/l | 2 |
| **Ni** | 0.0050 | 0 | 0 | 0 | 10 mg/l | 0.04 |
| **Sb** | 0.0050 | <0.0050 | 0 | 0.005 | - | 0.006 |
| **Pb** | 0.0200 | 0 | 0 | <0.0200 | 50 mg/l | 0.05 |
| **Cd** | 0.0020 | 0 | 0 | 0 | 5 mg/l | 0.004 |
| **Cu** | 0.0050 | <0.0050 | 0.008 | <0.0050 | 0.05 mg/l | 0.2 |
| **Zn** | 0.0050 | 0 | <0.0050 | 0 | 3 mg/l | 0.4 |
| **Cr** | 0.0050 | 0 | <0.0050 | 0 | 50 mg/l (tot) | 0.05 (tot) |
| **Se** | 0.0200 | <0.0200 | <0.0200 | 0 | 10 mg/l | 0.01 |
| **As** | 0.0200 | <0.0200 | 0 | <0.0200 | 50 mg/l | 0.05 |
| **Mo** | 0.0079 | <0.0079 | <0.0079 | <0.0079 | - | 0.05 |

### *3.4 Density measurement*

The volumetric mass density of representative samples of the materials analysed was determined by helium pycnometer. The results in Table 3.4 show the typical density values for calcareous rocks.

**Table 3.4.** Density measurement of the selected fractions of Orosei Marble waste.

| Sample | density [g/cm$^3$] |
|---|---|
| **CSG** | 2.72 |
| **CFP** | 2.67 |
| **CC** | 2.72 |

### *3.5 Moisture content*

The moisture content was determined in agreement with UNI EN 1097-5:2008. The determination of the water content was carried out by drying the samples of each typology in a ventilated oven (t=110 ± 5°C) . Successive weightings at fixed intervals (1 hour, 4 hours, 12 hours, 24 hours, 48 hours, and 72 hours) were undertaken to determine the constant mass of the dried test portion. From the data reported in Table 3.5, it can be clearly pointed out that the CFP sample has significantly more moisture content, due to its provenance from the filter press.

**Table 3.5.** Moisture content of the selected fractions of Orosei Marble waste.

| **Sample** | **%** |
|---|---|
| **CSG** | 0.27 |
| **CFP** | 25 |
| **CC** | 0.13 |

### *3.6 Mineralogical analysis*

The mineral phases were identified by powdered X-ray diffraction (XRD) analysis, performed with a θ-2θ conventional diffractometer with Cu Kα radiation (1.5418 Å). Appropriate quantities of each sample were lightly ground in agate mortar and packed into the sample holder.

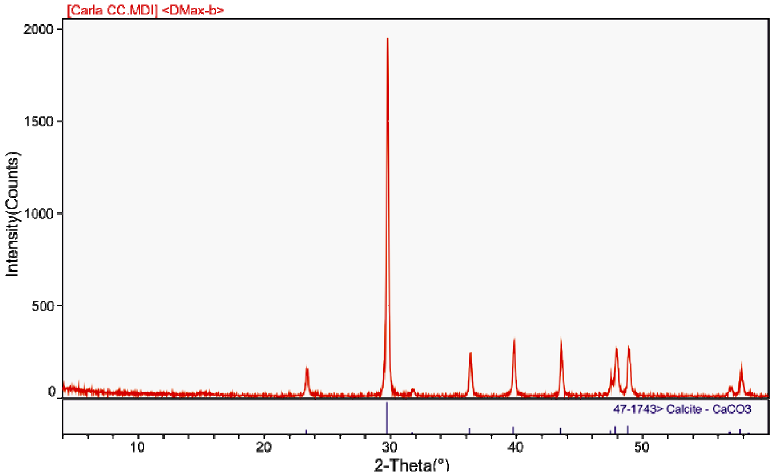

**Figure 3.5.** XRD Pattern of rejected stone fragments and trimmings (CC).

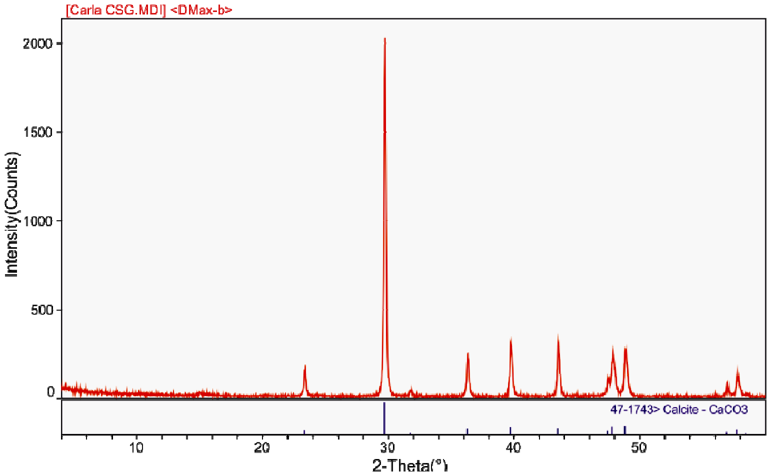

**Figure 3.6.** XRD Pattern of dust and fine powder (CSG).

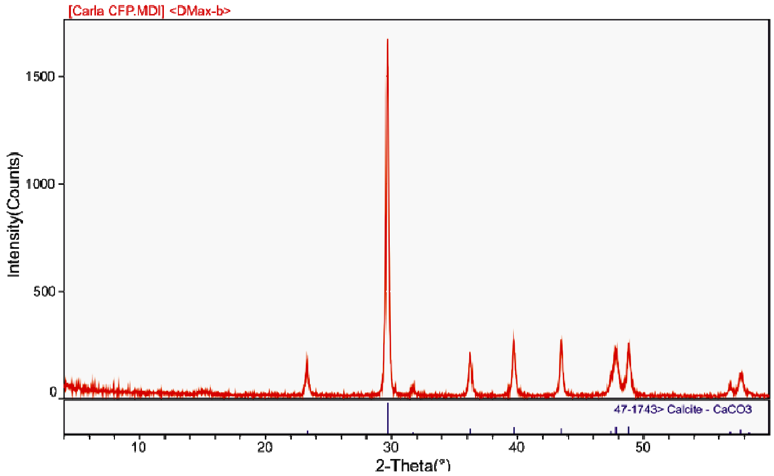

**Figure 3.7.** XRD Pattern of slurry from the filter press (CFP).

The XRD patterns (Figures 3.5, 3.6, 3.7) illustrate that the only mineral constituent detected is Calcite (or calcium carbonate, $CaCO_3$) for each of the three waste typologies considered. It is highly likely that the sample contains small amounts of other mineral phases, but reliable detection of minerals present in small amounts (below 1 or 2%) is difficult with XRD. The presence of calcite confirms the origin of this waste, stemming from calcareous stones.

According to this characterisation, each of the three waste typologies considered mainly consists of calcium carbonate. The chemical analyses of major and trace elements illustrated that hazardous elements, alkali and heavy metals are contained in negligible amounts. Furthermore, all concentrations are below legislation limits. By highlighting the absence of pollutants, it was demonstrated that their use is particularly suitable for commercial purposes.

To sum up, this stone waste may have a potential economic value and may be re-used for the production of mortars, henceforth called “ecological mortars” for their environmental-added value.

## *References*

P.L. Boar and I.K. Ingram (1970). The Comprehensive Analysis of Coal Ash and Silicate Rocks by Atomic-absorption Spectrophotometry by a Fusion Technique. Analyst, 95, 124-130.

Decreto Legislativo 3 aprile 2006, n. 152. Istituzione dell'elenco dei rifiuti, in conformità all'articolo 1, comma 1, lettera A), della direttiva 75/442/CE ed all'articolo 1, paragrafo 4, della direttiva 91/689/CE, di cui alla decisione della Commissione 2000/532/CE del 3 maggio 2000 *[Italian Decree of April 3, 2006, No.152: Establishment of a waste catalogue, in accordance with Article 1, paragraph 1, letter a) of Directive 75/442 / EC and Article 1, paragraph 4 of Directive 91/689 / EC, according to the decision of the Commission 2000/532 / EC of May 3, 2000]*.

D.M. Ambiente 5 aprile 2006, n.186: Regolamento recante modifiche al decreto ministeriale 5 febbraio 1998 «Individuazione dei rifiuti non pericolosi sottoposti alle procedure semplificate di recupero» *[Ministry of Environment - Italian Decree April 5, 2006, no. 186: Regulation amending Ministerial Decree February 5, 1998 «Identification of non-hazardous waste subject to simplified recovery procedures»]*.

D.M. Ambiente 27 settembre 2010: «Definizione dei criteri di ammissibilità dei rifiuti in discarica, in sostituzione di quelli contenuti nel decreto del Ministro dell'ambiente e della tutela del territorio 3 agosto 2005» *[Ministry of*

*Environment - Italian Decree September 27, 2010: «Definition of the criteria for acceptance of waste in landfills, replacing those contained in the Decree of the Minister of Environment and Protection of Land August 3, 2005»]*.

UNI EN 12457-2:2004. Characterisation of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).

UNI 8520-2:2005. Aggregati per calcestruzzo - Istruzioni complementari per l'applicazione della EN 12620 - Requisiti *[Aggregates for concrete - Additional instructions for the application of EN 12620 - Requirements]*.

UNI EN 1097-5:2008. Tests for mechanical and physical properties of aggregates. Determination of the water content by drying in a ventilated oven.

# Chapter 4. Preparation of the mortar mixtures and evaluation of their $CO_2$ absorption

After carrying out the analyses on the waste materials, and characterising them, the objectives of this part of the research were to prepare the most appropriate mixtures of the “ecological mortars” and test their carbon sequestration capacity.

Initially, the attention was focused on two commercial mortars in order that an appropriate experimental procedure could be established without having to deal with the waste materials. Afterwards, only after having conducted several experimental tests, a standard methodology was adopted and applied to the “ecological mortars” as well.

## *4.1 Commercial mortars*

### *4.1.1 Materials and methods*

In order to allow for materials which should be constituted of carbonate materials, namely high percentage of CaO, and have the same provenance of the waste object of the research, two of the most common commercial mortars in Sardinia (Italy) were selected. This initial analysis was conducted on common commercial mortars so as to establish a set of parameters to which subsequently compare the performance of the mortars constituted by stone waste. The first one, named CM, is a cement-based mortar, suitable for new buildings and reinforced concrete, which was prepared in compliance with EN 998-1:2010. The second mortar (LM) is a natural hydraulic lime mortar (NHL 3,5), suitable for ancient masonry buildings, and prepared in accordance with EN 459-1:2010.

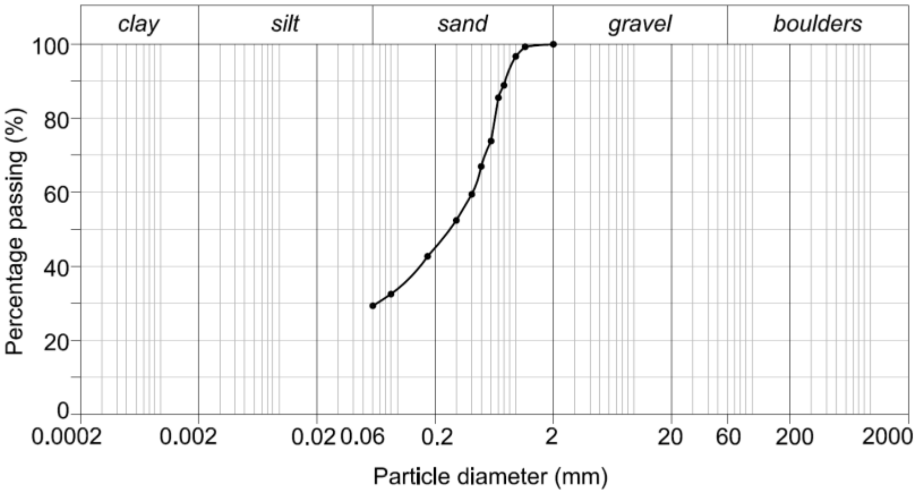

**Figure 4.1.** Grain size distribution of CM (cement mortar).

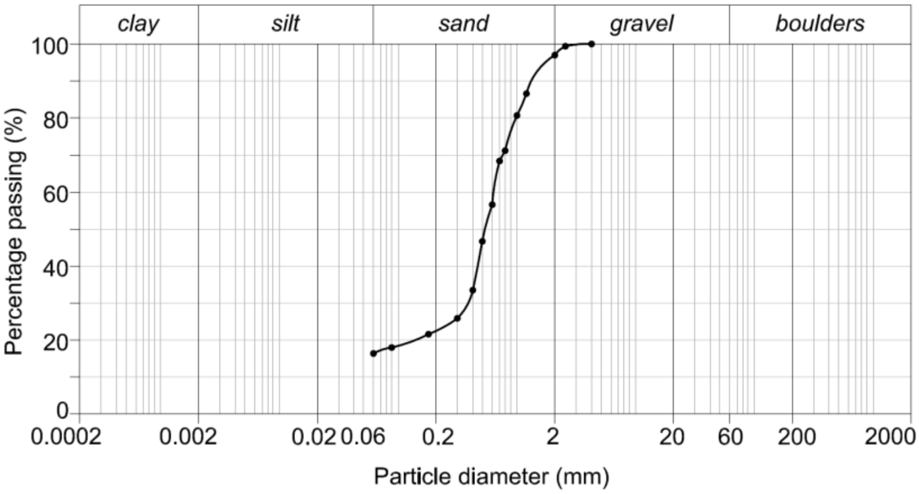

**Figure 4.2**. Grain size distribution of LM (natural hydraulic lime NHL 3.5).

Firstly, the grain size distribution of the commercial mortars was investigated so as to study their constituents as compared to those of the stone waste studied beforehand (Figures 4.1 and 4.2) as well as the chemical analysis and LOI determination of the aggregates used in the manufacture of the both cement- based and lime-based commercial mortars (Table 4.1).

**Table 4.1**. Comparison between the constituents of the commercial mortars and the stone waste – chemical analysis and LOI determination.

| **Analyte** | **CSG – dust and fine powder [%]** | **CFP – slurry from filter press [%]** | **CC – rejected stone fragments and trimmings [%]** | **aggregates of the commercial mortars (both cement- and lime-based mortars) [%]** |
|---|---|---|---|---|
| $Al_2O_3$ | 0.020 | 0.043 | 0.044 | 0.600 |
| $Fe_2O_3$ | 0.021 | 0.028 | 0.054 | 0.200 |
| MnO | 0.003 | 0.007 | 0.006 | - |
| MgO | 0.472 | 0.394 | 0.485 | 0.765 |
| $K_2O$ | 0.023 | 0.042 | 0.014 | 0.030 |
| $Na_2O$ | 0.035 | 0.053 | 0.050 | 0.010 |
| $TiO_2$ | 0.001 | 0.003 | 0.002 | - |
| $P_2O_5$ | 0.014 | 0.010 | 0.048 | - |
| $SiO_2$ | 3.386 | 3.455 | 0.250 | 0.720 |
| **CaO** | **51.650** | **49.830** | **54.720** | **54.254** |
| LOI | 43.650 | 44.550 | 43.960 | 43.410 |
| *Total* | *99.275* | *98.415* | *99.633* | *99.989* |

From the data it is evident that the elements making up the commercial mortars are strikingly similar to those constituting the waste object of this study, especially the rejected stone fragments and trimmings named CC.

The compressive strength of the commercial mortars was determined according to the standard EN 1015-11:1999/A1:2006 (EN 1015-11:1999/A1:2006 - Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar). Results are based on prisms made from the material cured and tested in accordance with the requirements of standard EN 998-1:2010 (EN 998-1:2010 - Specification for mortar for masonry. Rendering and plastering mortar). The compressive strength of the cement mortar and the hydraulic lime could be classified as CSII (1.5-5.0 N/mm$^2$) and CSI (0.4-2.5 N/mm$^2$), respectively.

Going into detail about the commercial mortars, the mineral composition was evaluated by powder XRD analysis, performed with a $\theta$-$2\theta$ conventional diffractometer with Cu Kα radiation (1.5418 Å) (Figure 4.3). An appropriate quantity of each sample was lightly ground in agate mortar and packed into the sample holder. The main crystalline phases detected in LM e CM resulted to be $CaCO_3$ (Calcite) and $Ca(OH)_2$ (Portlandite).

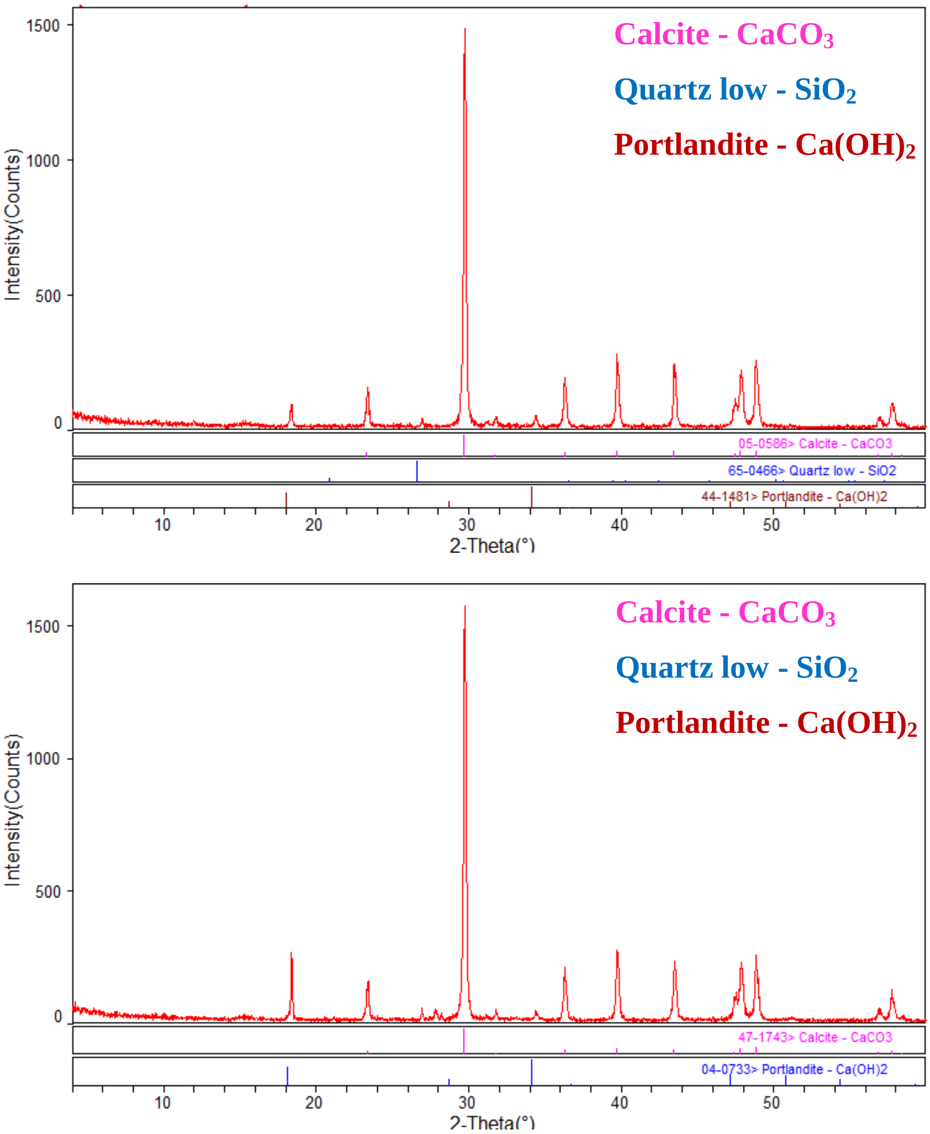

**Figure 4.3**. CM (above) and LM (below) XRD patterns.

CM and LM primary characteristics are reported in Table 4.2; the carbon dioxide required for the theoretically possible total carbonation of both CM and LM at 1 atm pressure of $CO_2$ was computed using the following formula (Steinour, 1959):

% $CO_2$ uptake [*min*]= $0{,}785CaO+0{,}91MgO+1{,}41Na_2O+0{,}935K_2O-0{,}55SO_3$

% $CO_2$ uptake [*max*]= $0{,}785CaO+(1{,}41/2)\ Na_2O+(0{,}935/2)\ K_2O-0{,}55SO_3$

The resulting percentage, fluctuating between 42% and 43.5% as far as CM is concerned and between 41.5% and 42% with reference to LM is in agreement with literature (Shtepenko et al., 2005; Kashef-Haghighi & Ghoshal, 2010).

**Table 4.2.** Chemical analysis and LOI determination.

| Analyte | CM [%] | LM [%] | Steinour uptake [g/kg] | CM | LM |
|---|---|---|---|---|---|
| $Al_2O_3$ | 0.37 | 0.71 | minimum | 424 | 415 |
| $Fe_2O_3$ | 0.12 | 0.40 | maximum | 435 | 422 |
| MnO | 0.01 | 0.02 | **Calcimetry [g]** | **CM** | **LM** |
| MgO | 0.75 | 1.13 | $CO_2$ | 0.139 | 0.149 |
| $K_2O$ | 0.07 | 0.12 | | | |
| $Na_2O$ | 0.03 | 0.09 | | | |
| $TiO_2$ | 0.02 | 0.03 | | | |
| $SiO_2$ | 2.46 | 2.78 | | | |
| CaO | 52.79 | 53.88 | | | |
| LOI | 43.59 | 41.61 | | | |

### *4.1.2 Experimental apparatus*

The $CO_2$ capture capacity of both CM and LM was experimentally appraised under standard ambient temperature and pressure conditions (SATAP: pressure = 1 bar, temperature = 25°C) using a modification of Mavor volumetric approach (Mavor, 1990) as described in literature (Ciccu et al., 2011; Mazzella, 2011; Mazzella et al., 2012).

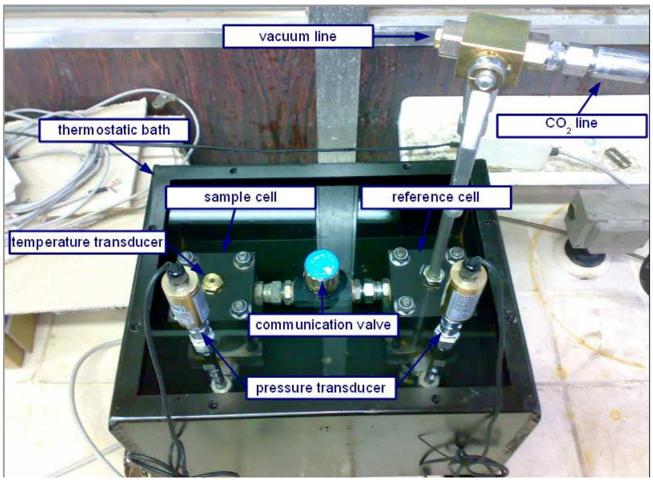

**Figure 4.4.** Experimental apparatus used for laboratory tests.

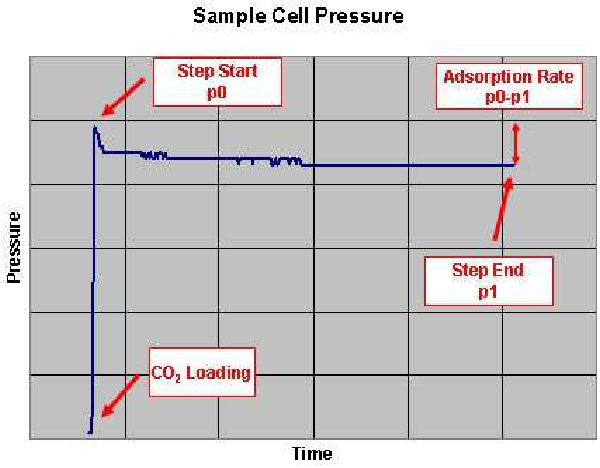

**Figure 4.5.** Pressure trend during a 24-hour test.

The experimental apparatus (Figure 4.4) consisted of a double 500 $cm^3$ stainless cell. Whilst one cell hosts the sample, the other one is a reference cell that serves as reservoir for the $CO_2$, also allowing an evaluation of the behaviour of the gas in the same conditions of the sample cell. The experimental apparatus is immersed in a thermostatic bath in order to keep the temperature steady during each test. Pressures and temperatures in both cells are independently monitored with high precision transducers with a sensitivity of 0.1 bar and 0.1 °C. All time-dependent data on pressure are collected with a personal computer at a rate of 1 point per second.

### *4.1.3 Experimental procedure*

In order that an assessment of the $CO_2$ uptake of both LM and CM can be carried out, an experimental procedure was designed as follows: 4 samples of both LM and CM were cast in four small cylindrical plastic moulds and immediately sealed with para-film paper to prevent early carbonation (Figure 4.6).

**Figure 4.6.** Preparation of mortars (left) and plastic moulds (right).

Of these four samples, three were tested respectively after 1, 7 and 28 days from their preparation and the fourth sample was kept sealed as a control, untreated sample. Each test were implemented at mild accelerated conditions, namely SATAP: temperature=25°C, pressure=1 bar, hence higher than $CO_2$ concentration in air (0.039% by volume).

The experimental measuring procedure was initiated bringing the experimental apparatus to under vacuum (in order to exclude the sequestration of atmospheric gases), charging the sample cell with 1 bar of $CO_2$ with a percentage by volume of approximately 99% and allowing the reaction between the $CO_2$ and the sample for 24 hours. At the end of the test, each sample was extracted from the apparatus, weighted, and analyzed by means of XRD technique and Dietrich-Fuller calcimetry.

The production of solid calcite as a result of carbonation brings about a dip in the pressure measured within the sample cell and recorded by the pressure transducers. This drop can be directly related to the amount of carbon that is sequestrated. On the basis of the observed pressure values, the amount of $CO_2$ at start and end of each test is calculated using the Soave modification of Redlich-Kwong (RKS) equation of state (Soave, 1972):

$$p=[(RT)/(\tilde{V}-b)] – [(a\alpha)/(\tilde{V}(\tilde{V}-b)]$$

*where*

*P: pressure [atm]*

*T: temperature [K]*

*R: ideal gas constant [l atm/K mol]*

$\tilde{V}$*: molar volume [*$cm^3$*/ n° mol]*

*a, b: chemical species constants (depending on critical p and t)*

$\alpha$*: acentric factor*

From the mass balance, the difference between the moles of $CO_2$ transferred from the reference cell and the moles of $CO_2$ calculated to be present in the sample cell at the final equilibrium condition are considered to be the adsorbed moles. The described procedure was repeated for curing day 1, 7, and 28 of both CM and LM.

Also, since carbonation is influenced by several factors such as temperature, relative humidity, carbon concentration into the atmosphere, porosity and free water content, a literature review on these parameters was conducted in order to identify the most suitable conditions. In particular, the following were taken into account:

- temperature: carbonation reaction rate increases with temperature;
- relative humidity (RH) of the air filling the pores: the moisture becomes vapour as long as RH<65%, whilst remains liquid water provided that RH>95% and is a combination of the two on condition that RH fluctuates between 65% and 95%. Concerning the effects on carbonation, it is more effective on mortars exposed to an environment where 50%<RH>70%. In fact, when RH>70%, pores start saturating with water slowing down the diffusion of $CO_2$ through the mortar, whereas in case RH<50%, the pores become dry impeding the dissolution of $Ca(OH)_2$ and $CO_2$ necessary for carbonation (RILEM, 2004).
- porosity: it is inversely proportional to mechanical properties (compressive and tensile strength). Also, it is modified by hydration reactions, which produce $Ca(OH)_2$ and C-S-H. Finally, as a result of carbonation, calcite precipitates on mortar pores, providing a fall in porosity and an increase in the density of carbonated areas of mortars, since calcite has higher molecular weight than portlandite (respectively 100.09 and 74.09) (Papadakis et al., 1991; Song & Kwon, 2007).

### *4.1.4 Results and discussion*

In order to quantify the actual percentage and to confirm RKS values of carbon capture, calcite content was determined through calcimetry analysis, conducted by putting 0.4 g of dried samples in a Dietrich-Fruehling apparatus, and adding 10 ml of HCl 1:1 v/v. In Table 4.3 the experimental results of carbon sequestration are reported both through RKS calculation and calcimetry analysis. From the data it can be demonstrated that both LM and CM are capable to take up $CO_2$. In particular, CM showed higher figures than LM. In comparison with Steinour's theoretical uptake, the uptake obtained through the 24-hour tests carried out is considerably lower; one possible reason for this could be that carbonation process starts from the preparation of mortars, lasts for all their service life, and even after their demolition, whilst the experimental procedure recorded the first 28 days of life of the mortars.

**Table 4.3.** Results of the experimental procedure.

| | **CM - cement mortar, EN 998-1:2003** | | | **LM - natural hydraulic lime NHL 3.5, EN 459-1:2010** | | |
|---|---|---|---|---|---|---|
| | ***day 1*** | ***day 7*** | ***day 28*** | ***day 1*** | ***day 7*** | ***day 28*** |
| total duration [h] | 24 | 24 | 24 | 24 | 24 | 24 |
| temperature [°C] | 25 | 25 | 25 | 25 | 25 | 25 |
| RH [%] | 55 | 55 | 55 | 56 | 56 | 56 |
| Pressure range [Bar] | 0.1-1 | 0-1 | 0-1 | 0.8-1 | 0.7-1 | 0.4-1 |
| weight pre [g] | 32.22 | 32.74 | 32.38 | 35.32 | 33.78 | 34.90 |
| weight post [g] | 32.82 | 33.14 | 33.28 | 35.42 | 33.88 | 35.30 |
| weight gain [g] | 0.60 | 0.40 | 0.90 | 0.10 | 0.10 | 0.40 |
| **RKS $CO_2$ uptake [g$CO_2$/kg mortar]** | **19.11** | **25.49** | **26.35** | **4.99** | **11.00** | **16.04** |
| **Calcimetry $CO_2$ variation [g $CO_2$/kg mortar]** | **15.62** | **24.01** | **27.45** | **2.38** | **13.72** | **18.10** |

Figure 4.7 illustrates that the cement mortar has a pattern similar to a plateau during the 28 days considered, whilst the hydraulic lime has a virtually linear increase in the same period.

Additionally, it is possible to note in Figure 4.8 that a faster decrease in pressure for each experimental day was detected as far as CM is concerned.

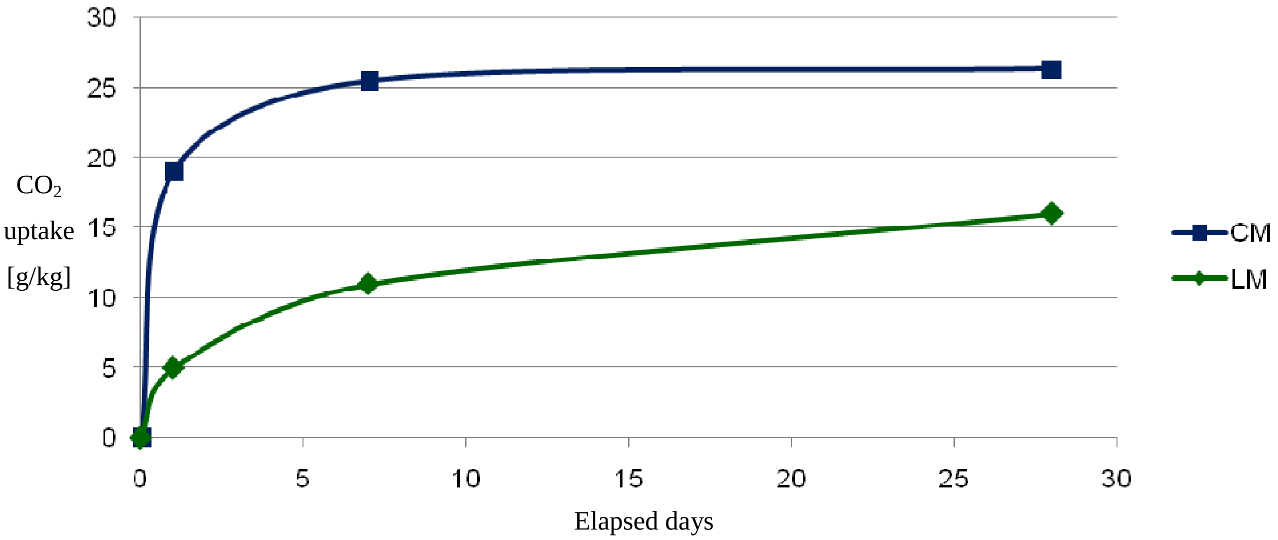

**Figure 4.7**. Carbon uptake trend for the first 28 days of curing.

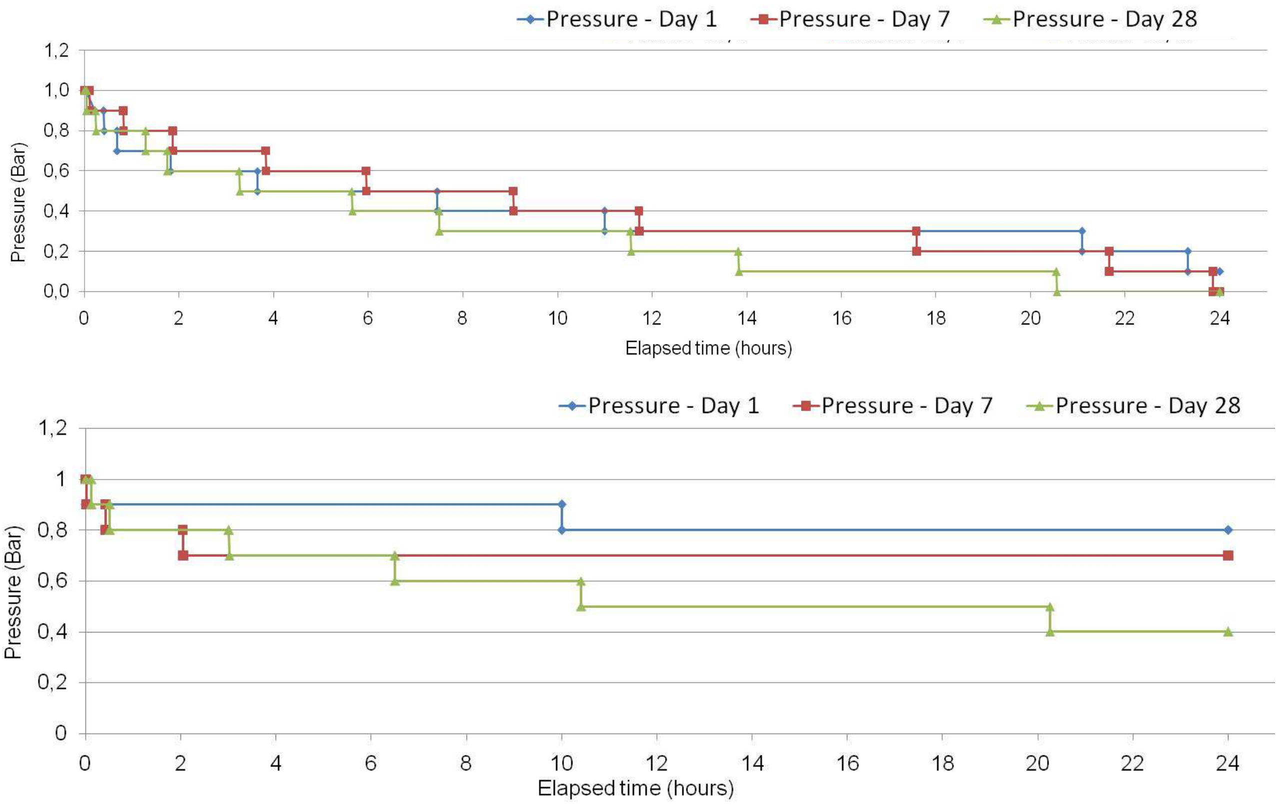

**Figure 4.8**. Pressure variations in time: CM (above) and LM (below).

After having unmoulded, divided into two halves and crushed the samples to powder using a mortar and pestle (Figure 4.9), some ex-post analyses on the untreated and treated samples were performed in order to quantify the actual percentage of $CO_2$ reabsorbed. In particular, the following were carried out:

- phenolphtalein test;
- X-ray diffraction;
- petrographic analysis.

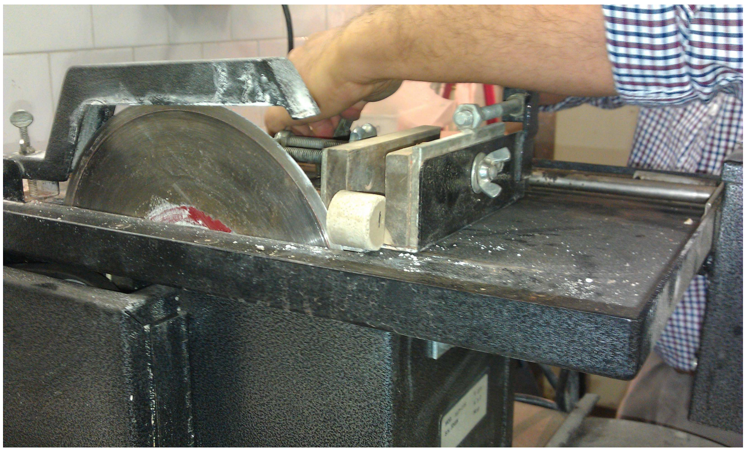

**Figure 4.9**. Saw cutting of the samples.

The phenolphtalein test was undertaken according to a standard implemented by the International Union of Laboratories and Experts in Constructions Materials, Systems and Structures (RILEM, 1988). It involves the use of a solution 1% phenolphtalein in 70% ethyl alcohol to indicate the changes in pH owing to carbonation. Indeed, carbonation leads to a reduction of the pH-value of the pore solution to less than 9. The specimens were sprayed with indicator solution, which turns non-carbonated areas red, whereas it remains colourless in carbonated areas.

Since the results depend on cutting procedure, during the tests it was pointed out that saw-cuts not always lead to an appropriate assessment of the carbonation depth of the samples, as showed in Figures 4.10 and 4.11. In fact, regarding CM, a certain carbonation degree is evident in samples #2, #3, #4, and yet the saw-cut somewhat provoked negative consequences on the sample surfaces #5 and #6, which are untreated samples, hence they ought to be red (Figure 4.10).

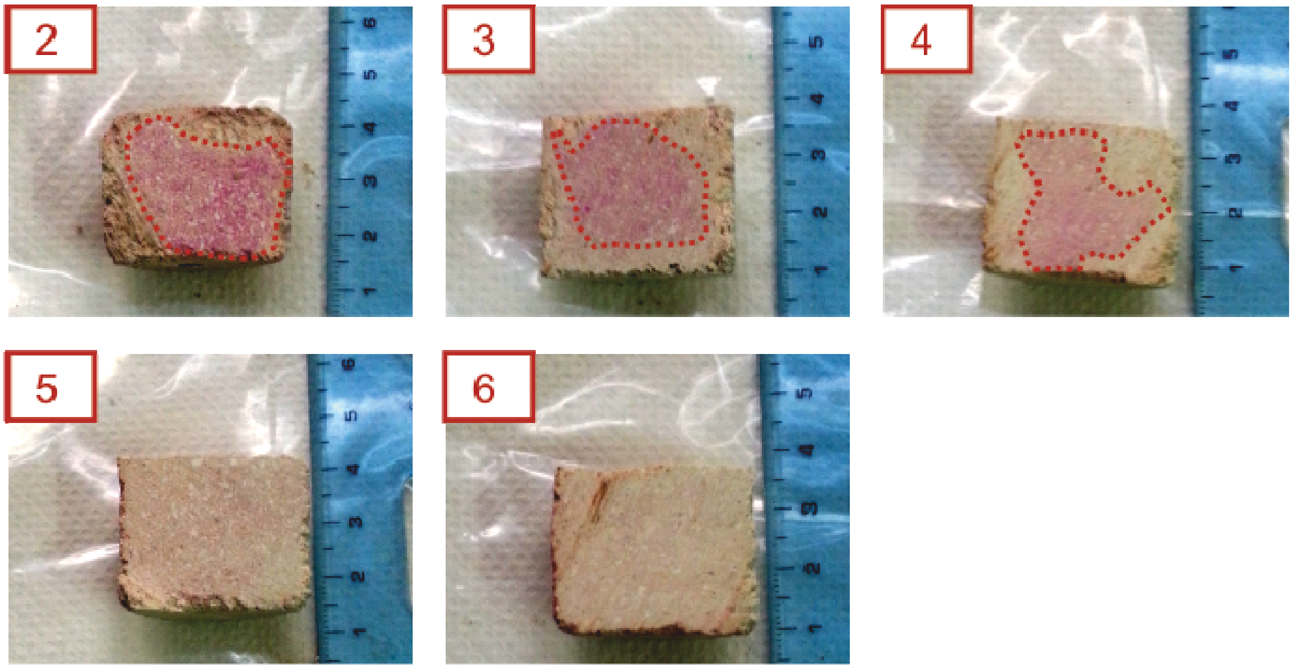

**Figure 4.10.** Phenolphtalein test on the CM samples #2, #3, #4 (treated), and #5 #6 (untreated).

As well as CM, phenolphtalein test on LM poses the same problems. To the left of Figure 4.11 it is showed a treated sample, which has the upper side colourless (hence carbonated), whilst to the right an untreated sample is displayed. However, it is possible to note how saw-cutting makes it extremely difficult to interpret correctly the phenolphtalein test.

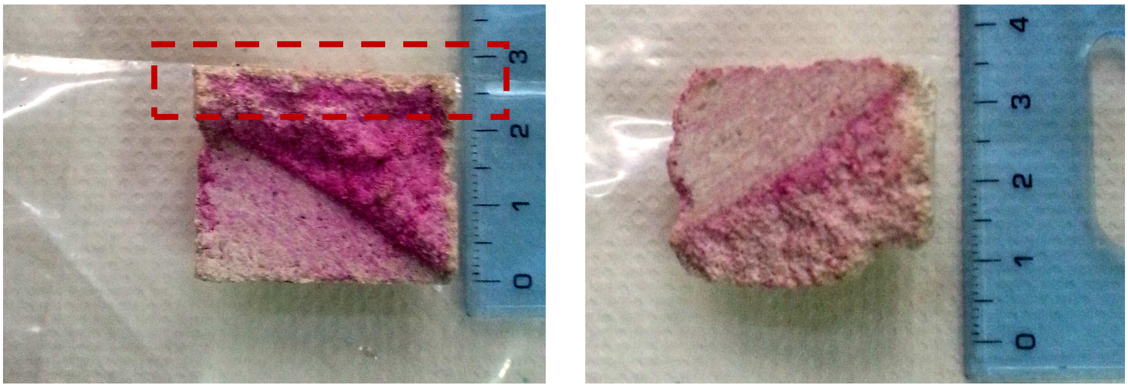

**Figure 4.1.** Phenolphtalein test on the LM samples (left: treated; right: untreated).

Therefore, it is required to perform further analyses in order to obtain a more precise evaluation of the occurred carbonation.

X-ray diffraction and microscopy analyses on the untreated and treated samples were performed so as to evaluate structural modifications of both CM and LM as a result of the $CO_2$ uptake. XRD analyses (Figures 4.12 and 4.13) were conducted through Rigaku Geigerflex diffractometer, using CuKα radiation ($\lambda Cu = 1.54178$ Å).

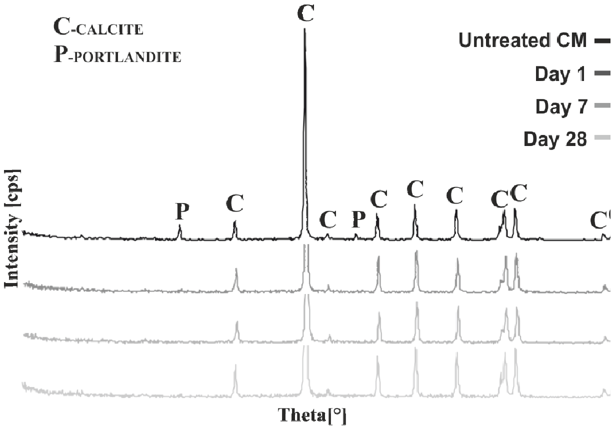

**Figure 4.12.** XRD patterns of untreated and treated CM.

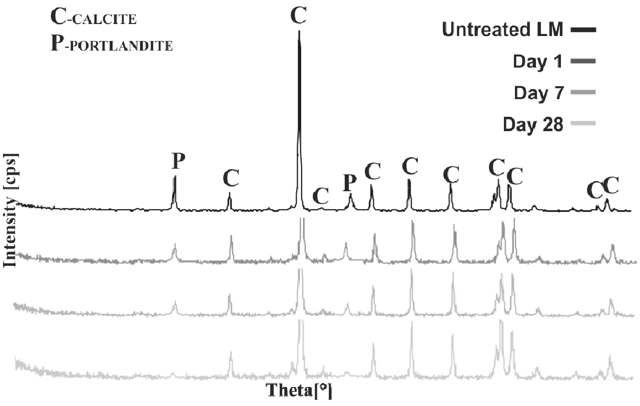

**Figure 4.13.** XRD patterns of untreated and treated LM.

These analyses highlighted, as it can be expected, that whilst portlandite peaks disappeared, as a result of the reaction between gaseous $CO_2$ and the CM and LM matrix, a growth in calcite peaks was appreciated, due to its higher concentration in the sample. The petrographic study was conducted after preparing thin sections, which were studied by means of a polarizing microscope in transmitted light. The pore structure was measured through digital image analysis technique with Image J 1.47v Software Package.

Concerning the porosity of cement-based and lime-based mortars, literature on the subject identifies three values: total porosity (the fraction of the total volume that is occupied by pores), pore size distribution (the fraction of total pore volume in which the pores lie within a stated size range) and specific surface (the area or accessible surface area contained in unit mass of volume of solid) (RILEM, 2004; Elsen, 2006; Song and Kwon, 2007). However, since the mortar itself is constituted by a porous binder along with aggregates which can also be porous, the determination of the porosity of a mortar could be particularly difficult. Moreover, even though the porosity is determined in the first phase, the hardening, the subsequent drying process could affect it and finally it is influenced by the carbonation process. In fact, the reduction in porosity was associated with the carbonation degree (Ishida et al, 2004), whilst the infiltration of calcium oxide through layers beyond the carbonation front, and the simultaneous precipitation of calcite into the carbonated layer was identified as a mechanism by means of which the porosity decreases (Bary and Sellier, 2004), producing ring-like structures of calcite along the interior of the voids (Ishida et al., 2004).

Literature identified several techniques to evaluate porosity in cement-based and lime-based materials. There are direct and indirect methods: according to the former, the porosity is assessed by direct observation; as far as the latter is concerned, the porosity is deduced from measurements. Indeed, the same sample could report different figures of porosity according to the different techniques.

In this work, the porosity was measured according to Computerised Digital Image Analysis, combined with a polarizing microscope in transmitted light. A digital camera attached to the microscope was used, allowing the capture of an image, composed of pixels, of the thin sections. Each pixel defined a point in the image for which the position and grey scale value or colour is known. Thus, these pixels were classified and grouped according to criteria established by the operator, namely in order to give the pore percentage that was displayed in the image.

For both mixtures, the aggregate composition consisted of carbonatic fragments distinctly identifiable (calcite-sparite), whilst with reference to the aggregate morphology an angular and elongated shape of the grains, and a low sphericity were noted. Also, the aggregates were well sorted, demonstrating a similar size range.

These analyses underlined that, for both CM and LM, $CO_2$ uptake occurred in the pores, in which calcite crystals had precipitated. Also, the comparison between the thin sections of untreated and treated samples (Figure 4.14) pointed out that, as a consequence of carbonation, a ring structure of calcite was determined, confirming the literature. Once calcite crystals have occluded the pore, $CO_2$ was allowed to flow through the fractures into the mortar matrix, reacting with calcium hydroxide and silicates, and precipitate as calcium carbonate.

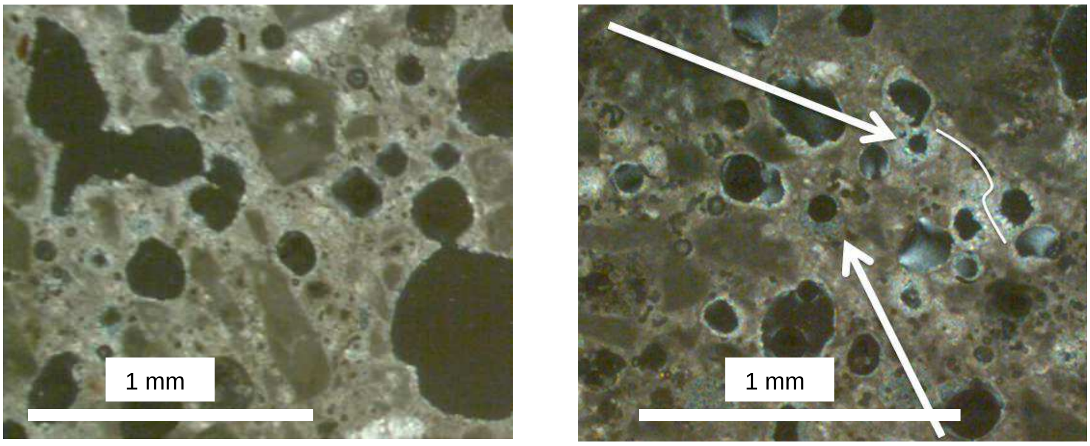

**Figure 4.14.** Comparison between untreated (left) and treated CM (right).

Furthermore, as far as the hydraulic lime (LM) is concerned, a decrease from 14% to around 5% was observed in the porosity of the 28th day sample as compared to the sample of the first day of curing, due to the presence of calcite along the interior of voids, as a result of calcite precipitation after carbonation (Figure 4.15).

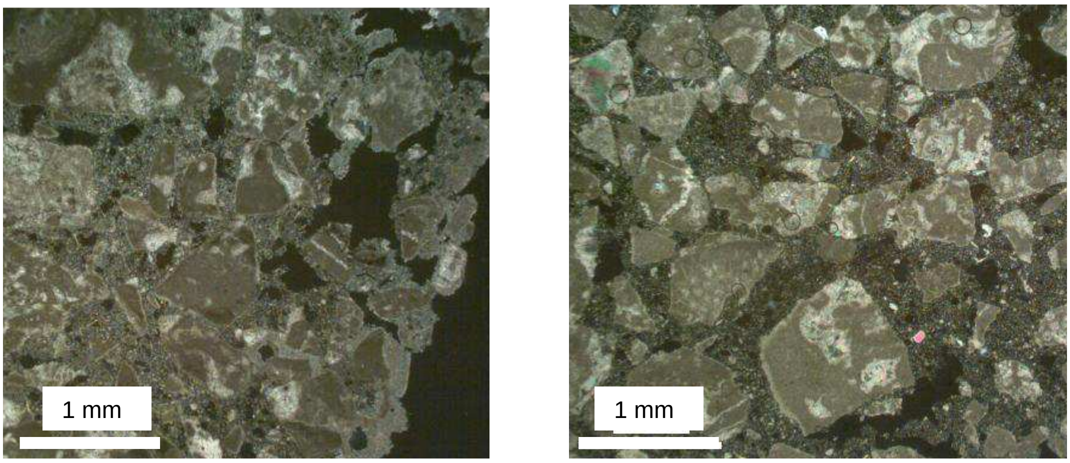

**Figure 4.15.** Some of the several thin sections comparing the 1st day sample (left) with the 28th day sample (right) of LM.

Overall, a decrease in porosity was noticed for both mixtures, as reported in Table 4.4 and Figure 4.16.

In sum, the preliminary results demonstrated that carbon uptake by common mortars during their curing time is not negligible. Although $CO_2$ sequestration figures appreciated are far from the performance of other materials, such as coal ash and industrial residues, it should be pointed out, however, that mortars have great potential, since their use in construction industry and, consequently, in all built-up environments is impressively widespread. In fact, low though they may seem, these values could represent a significant amount considering the entire period of service life, and afterwards, notably after demolition of mortars.

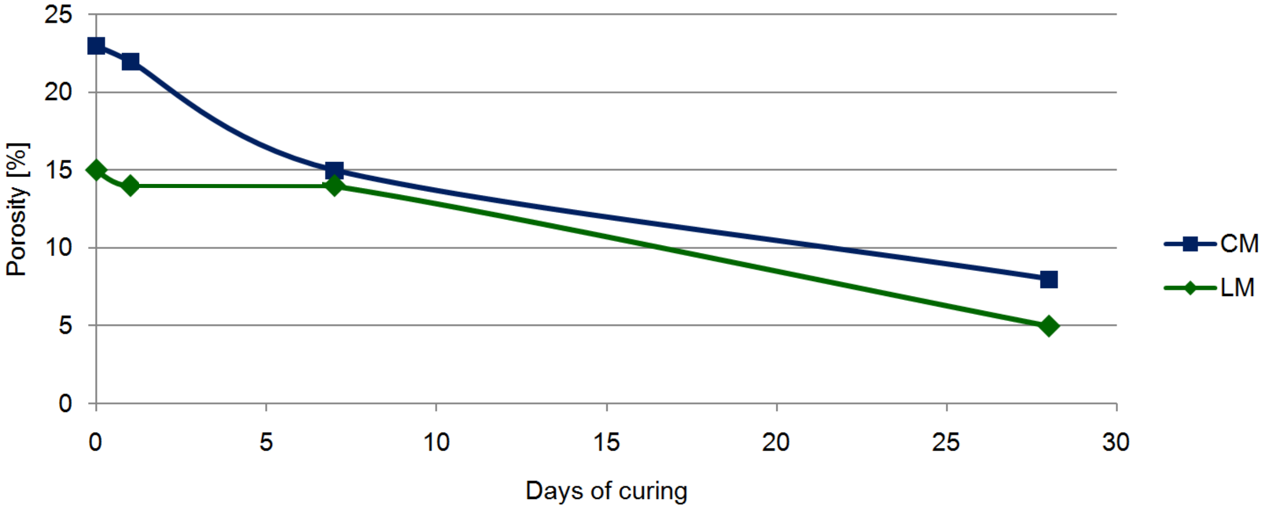

**Figure 4.16**. Observed decrease in the porosity of the cement mortar and the hydraulic lime in the curing period of 28 days.

**Table 4.4.** Porosity figures of the cement mortar and the hydraulic lime in the curing period of 28 days.

| | **Porosity [%]** |
|---|---|
| **CM - untreated** | 23 |
| **CM - day 1** | 22 |
| **CM - day 7** | 15 |
| **CM - day 28** | 8 |
| | |
| **LM - untreated** | 15 |
| **LM - day 1** | 14 |
| **LM - day 7** | 14 |
| **LM - day 28** | 5 |

## *4.2 Ecological mortars*

After having studied the main features distinguishing the commercial mortars and established a methodology through which conduct the experimental procedure, this part of the research was focused on the preparation of the "ecological mortars" and the assessment of their specific $CO_2$ absorption. Moreover, a further scope was the comparison with the $CO_2$ uptake of the commercial mortars previously characterised.

### *4.2.1 Materials and methods*

As after a curing time of 28 days the commercial lime mortar (LM) reported an almost linear increase, suggesting slower setting and hardening, there appears to be some evidence that in this mortar there is room for further carbonation. Therefore, lime was chosen to be the binder constituent of the "ecological mortars". In particular, non-hydraulic lime, also known as either hydrated lime or putty lime, was selected for the following reasons:

- its use in thin layers is commonly widespread as external and internal plaster owing to its plasticity and good vapour exchange. Indeed, its flexibility and permeability provides masonry with higher breathability, that is the ability of a building to allow vapour to be transmitted through the material. For this reason, lime mortars may be used both in new constructions and conservation projects, raising the possibility for more sustainability in the building industry.
- it is typically used in the most external layer of a plaster, thus in direct contact with the air.

Lime plaster is a mixture of water, calcium hydroxide and sand. According to the EN 459-1: 2010 standard, this type of lime is classified as Calcium Lime, codes CL90, CL80 or CL70 depending on the percentage of calcium and magnesium oxides, respectively at least 90%, 80%, and 70%. Hydrated lime is a air binder, meaning that it is a non-hydraulic lime and it do not set in contact with water; it can only set by reaction with carbon dioxide in the atmosphere through carbonation, which implies the absorption of $CO_2$. It causes the plaster to set by transforming once again the calcium hydroxide into calcite (calcium carbonate).

Consequently, it was chosen to manufacture a number of experimental mortar mixtures using the fractions of stone waste previously collected utilising lime as the binder component. Therefore, the “ecological mortars” are lime plasters indeed.

A lime putty CL 90 prepared in compliance with EN 459-1: 2010 was selected, being made up of the components reported in Table 4.5.

**Table 4.5.** Chemical analysis of the lime putty.

| **Analyte** | **[%]** |
|---|---|
| CaO+MgO | 98.400 |
| MgO | 0.740 |
| $CO_2$ | 0.720 |
| $SO_3$ | ≤2 |
| **Total** | **99.860** |

**Figure 4.17.** Preparation of lime putty (left) and collection of CFP (right).

Initially, two mixtures (Mixtures A and B) were prepared by mixing water, lime putty and the CFP (namely slurry from filter press from the Orosei Marble waste, Figure 4.17) fraction of the waste characterised before.

A preliminary examination of mix proportions and compressive strengths was undertaken, resulting in the figures reported in Table 4.6. In Figure 4.18, the differences in colours between the mixtures are displayed.

**Table 4.6.** Mix proportions of the Mixtures A and B.

| **ID mix** | **constituents** | **[g]** | **[ml]** | **water content** | **proportions stone waste/ lime putty** |
|---|---|---|---|---|---|
| **A** | water | 22.05 | 22.05 | - | 1:1 |
| | lime putty | 672.91 | 500 | 54% | |
| | CFP | 448 | 500 | 15% | |
| **B** | water | 126 | 126 | - | 4:1 |
| | lime putty | 265.57 | 200 | 54% | |
| | CFP | 817.85 | 800 | 15% | |

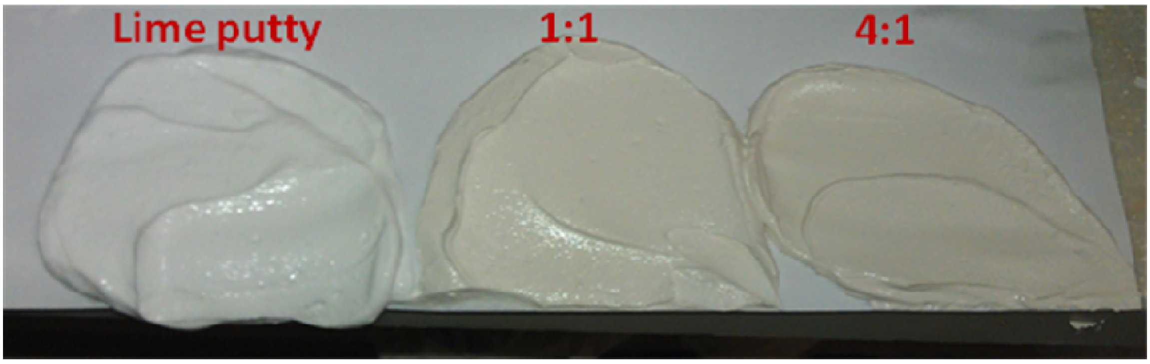

**Figure 4.18**. Colour distinction between the mixtures as compared to lime putty.

In connection with the compressive strengths, a resistance test according to the standard EN 1015-11:1999/A1:2006 (EN 1015-11:1999/A1:2006 - Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar) was performed on the hardened products.

**Figure 4.19.** Mixture hardening.

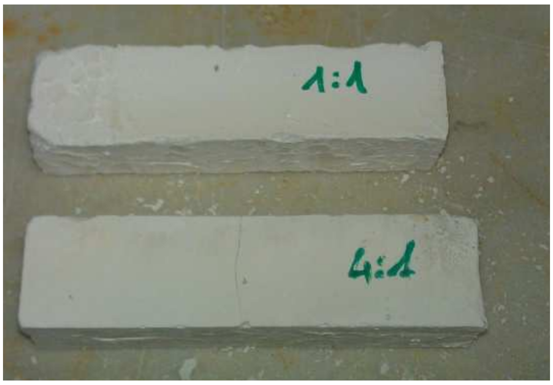

**Figure 4.20.** Hardened and unmoulded mixtures.

Results are based on prisms made from the material cured and tested in accordance with the requirements of standard EN 998-1:2010 (EN 998-1:2010 - Specification for mortar for masonry. Rendering and plastering mortar) (Figures 4.19 and 4.20). The classification provided by this standard is reported in Table 4.7.

**Table a.** Classification of mortar strengths according to EN 998-1:2010.

| **EN 998-1 mortar class** | **CSI** | **CSII** | **CSIII** | **CSIV** |
|---|---|---|---|---|
| Compressive strength after 28 days [N/mm$^2$] | 0.4 - 2.5 | 1.5 - 5.0 | 3.5 - 7.5 | ≥ 6.0 |

This type of classification is based on the performance of the mortars. The standard includes two primary typologies of mortars: GP - General purpose mortar for internal/external render (EN 998-1) and T - Masonry mortar with guaranteed performance, applied in thin layers for internal and external applications (EN 998-2). As far as the former type is concerned, it does not have structural use, thus the strength requirements are less demanding as compared to those of cement for concrete production, as an example. In particular, the production company ought to test the performance of the mortar and afterwards declare its class according to the aforementioned standard.

In accordance with the results of compressive tests shown in Table 4.8, both mixtures could be classified as GP - General purpose mortar for internal/external render (EN 998-1) and CSI (0.4-2.5 N/mm$^2$).

**Table 4.8**. Results of compressive tests on Mixtures A and B.

| **ID mix** | | **Dimensions [cm]** | **Surface [cm$^2$]** | **Results (EN 1015-11)** | | |
|---|---|---|---|---|---|---|
| | | | | ***Curing day*** | ***Applied force [kN]*** | ***Breaking load [N/mm$^2$]*** |
| 1:1 | A1 | 4X4X16 | 16 | 28 | 3.02 | 1.886 |
| | | | | | 3.03 | 1.887 |
| | A2 | | | | 3.85 | 1.980 |
| | | | | | 3.95 | 1.990 |
| 4:1 | B1 | 4X4X16 | 16 | 28 | 1.49 | 0.932 |
| | | | | | 2.66 | 1.664 |
| | B2 | | | | 2.56 | 1.599 |
| | | | | | 2.60 | 1.618 |

In light of the previous mixtures, other mix designs were prepared so as to better simulate mortars in their service by adding to water and lime putty an amount of the crushed CC fraction (notably rejected stone fragments and trimmings from the Orosei Marble waste) of the waste characterised in the first phase of the research. Moreover, so as to compare the performance of the stone waste object of this study with that of the internationally famous stone extracted from the Apuan Alps in Tuscany, an additional mixture was manufactured by utilising crushed Apuan Marble. Hence, Mixture C consisted of water, lime putty and crushed rejected stone fragments and trimmings from Apuan Marble waste, whilst Mixture D was made up of water, lime putty and crushed rejected stone pieces from Orosei Marble waste, both prepared in a ratio between stone waste and lime putty of 3:1. The comparison between the constituents of Apuan and Orosei Marble waste is provided in Table 4.9.

**Table 4.9**. Comparison between the constituents of Apuan and Orosei Marble waste.

| **Analyte** | **Rejected stone fragments and trimmings from Apuan marble waste [%]** | **Rejected stone fragments and trimmings from Orosei marble waste [%]** |
|---|---|---|
| $Al_2O_3$ | 0.035 | 0.044 |
| $Fe_2O_3$ | 0.016 | 0.054 |
| MgO | 0.837 | 0.485 |
| $K_2O$ | 0.014 | 0.014 |
| $Na_2O$ | 0.046 | 0.050 |
| $SiO_2$ | 0.275 | 0.250 |
| CaO | 55.020 | 54.720 |
| LOI | 44.090 | 43.960 |
| Total | 100.333 | 99.633 |

Also, for both Mixtures C and D, two additional mix-designs were manufactured: a finer one, namely constituted by aggregates of fine grain size (samples C1 and D1), and a coarser one, formed by aggregates of fine and medium grain size (samples C2 and D2) (Tables 4.10 and 4.11). The reason behind this lies on the possibility of better simulate a common plaster in exercise, which is made of several different layers with the most external one being the finer. In fact, the samples of each mixture were composed of two parts: a layer of the finer mixture for the first 5 millimetres of depth and the medium mixture for the remainder of the specimen (45 mm) (Figures 4.21 and 4.22).

**Table 4.10**. Mixture C – Apuan Marble Waste mix designs.

| **ID mix** | **constituents** | **[g]** | **water content** | **proportions stone waste/ lime putty** |
|---|---|---|---|---|
| **C1 “fine”** | water | 250 | - | 3:1 |
| | lime putty | 1000 | 54% | |
| | Apuan marble waste – fine grain size (0 mm – 0.7 mm) | 3000 | - | |
| **C2 “medium”** | water | 350 | - | 3:1 |
| | lime putty | 1000 | 54% | |
| | Apuan marble waste – fine grain size (0 mm – 0.7 mm) | 1500 | - | |
| | Apuan marble waste – medium grain size (0.8 mm – 1.2 mm) | 1500 | - | |

**Table 4.11**. Mixture D – Orosei Marble Waste mix designs.

| ID mix | constituents | [g] | water content | proportions stone waste/ lime putty |
|---|---|---|---|---|
| **D1 “fine”** | water | 467 | - | 3:1 |
| | lime putty | 1000 | 54% | |
| | CC (Orosei marble waste) fine grain size (0 mm – 0.4 mm) | 3000 | - | |
| **D2 “medium”** | water | 300 | - | 3:1 |
| | lime putty | 1000 | 54% | |
| | CC (Orosei marble waste) fine grain size (0 mm – 0.4 mm) | 1500 | - | |
| | CC (Orosei marble waste) medium grain size (0.8 mm – 1.4 mm) | 1500 | - | |

**Figure 4.21**. Preparation of the mixtures (left and middle) and a sample (right).

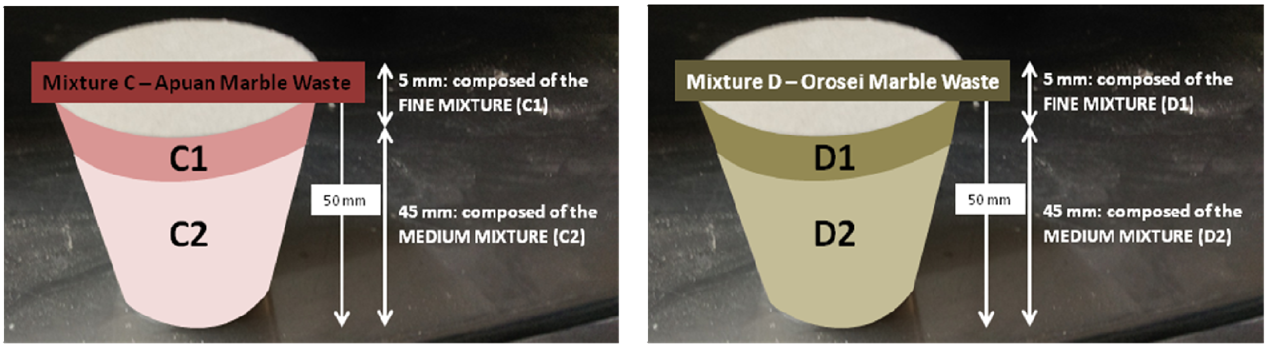

**Figure 4.22**. Sample structure.

Also, compressive strengths were also undertaken on Mixtures C and D (Tables 4.12-4.15). According to the aforementioned standard, once again both mixtures could be classified as GP - General purpose mortar for internal/external render (EN 998-1) and CSI (0.4-2.5 N/mm$^2$).

**Table 4.12**. Results of compressive tests on Mixture C1 “fine”.

| **ID sample** | **Dimensions [cm]** | **Surface [cm$^2$]** | **Results (EN 1015-11)** | | |
|---|---|---|---|---|---|
| | | | ***Curing day*** | ***Applied force [kN]*** | ***Breaking load [N/mm$^2$]*** |
| a | 4x4x16 | 16 | 28 | 1.8 | 1.182 |
| | | | 28 | 1.6 | 0.974 |
| b | | 16 | 28 | 1.6 | 0.962 |
| | | | 28 | 1.5 | 0.925 |
| c | | 16 | 28 | 1.4 | 0.875 |
| | | | 28 | 1.6 | 1.019 |

**Table 4.13**. Results of compressive tests on Mixture C2 “medium”.

| **ID sample** | **Dimensions [cm]** | **Surface [cm$^2$]** | **Results (EN 1015-11)** | | |
|---|---|---|---|---|---|
| | | | ***Curing day*** | ***Applied force [kN]*** | ***Breaking load [N/mm$^2$]*** |
| a | 4x4x16 | 16 | 28 | 1.8 | 1.122 |
| | | | 28 | 1.6 | 1.005 |
| b | | 16 | 28 | 1.8 | 1.098 |
| | | | 28 | 1.8 | 1.142 |
| c | | 16 | 28 | 1.8 | 1.112 |
| | | | 28 | 1.6 | 1.001 |

**Table 4.14**. Results of compressive tests on Mixture D1 “fine”.

| **ID sample** | **Dimensions [cm]** | **Surface [cm$^2$]** | **Results (EN 1015-11)** | | |
|---|---|---|---|---|---|
| | | | ***Curing day*** | ***Applied force [kN]*** | ***Breaking load [N/mm$^2$]*** |
| a | 4x4x16 | 16 | 28 | 1.9 | 1.176 |
| | | | 28 | 1.5 | 0.968 |
| b | | 16 | 28 | 1.6 | 0.980 |
| | | | 28 | 1.5 | 0.906 |
| c | | 16 | 28 | 1.4 | 0.882 |
| | | | 28 | 1.6 | 1.029 |

**Table 4.15**. Results of compressive tests on Mixture D2 “medium”.

| **ID sample** | **Dimensions [cm]** | **Surface [$cm^2$]** | **Results (EN 1015-11)** | | |
|---|---|---|---|---|---|
| | | | ***Curing day*** | ***Applied force [kN]*** | ***Breaking load [$N/mm^2$]*** |
| a | 4x4x16 | 16 | 28 | 1.8 | 1.115 |
| | | | 28 | 1.6 | 1.017 |
| b | | 16 | 28 | 1.8 | 1.115 |
| | | | 28 | 1.8 | 1.151 |
| c | | 16 | 28 | 1.8 | 1.115 |
| | | | 28 | 1.6 | 1.004 |

On completion of the preparation of the lime plasters, 3 samples of each mixture underwent carbonation tests under mild accelerated conditions performed in curing days 1, 7, and 28 through the methodology previously established for the commercial mortars, using the aforesaid experimental apparatus and calculating the $CO_2$ absorption through the Soave modification of Redlich-Kwong (RKS) equation of state. As well as the commercial mortars, a fourth sample was sealed and considered as untreated one.

### *4.2.2 Results and discussion*

RKS values of carbon sequestration are reported in comparison with the values provided by the calcimetry analysis in Table 4.16.

**Table 4.16.** Results of the experimental procedure on Mixtures C and D.

| | **Mixture C – Apuan Marble Waste** | | | **Mixture D – Orosei Marble Waste** | | |
|---|---|---|---|---|---|---|
| | ***day 1*** | ***day 7*** | ***day 28*** | ***day 1*** | ***day 7*** | ***day 28*** |
| total duration [h] | 24 | 24 | 24 | 24 | 24 | 24 |
| temperature [°C] | 25 | 25 | 25 | 25 | 25 | 25 |
| RH [%] | 55 | 55 | 55 | 55 | 55 | 55 |
| Pressure range | 0.8-1 | 0-1 | 0-1 | 0.9-1 | 0.4-1 | 0.3-1 |
| weight pre [g] | 131.72 | 119.42 | 114.67 | 126.13 | 113.08 | 104.92 |
| weight post [g] | 131.74 | 120.52 | 115.43 | 126.14 | 113.57 | 105.66 |
| weight gain [g] | 0.02 | 1.10 | 0.76 | 0.01 | 0.49 | 0.74 |
| **$CO_2$ uptake [$gCO_2/kg$]** | **1.70** | **10.83** | **9.24** | **0.85** | **7.39** | **11.19** |
| **Calcimetry $CO_2$ variation [g $CO_2$/kg mortar]** | **1.81** | **13.71** | **9.00** | **0.45** | **6.83** | **11.33** |

From the data it can be seen that both mixtures managed to absorb carbon dioxide. However, Mixture D showed an upward trend during the period considered, whilst the uptake of Mixture C slowed down in the 28th curing day. The differences between the behaviour of the two mixtures are clearly evident in the graph reported in Figure 4.23, with Mixture C dropping after the seventh day of mortar curing and the Mixture D on the increase.

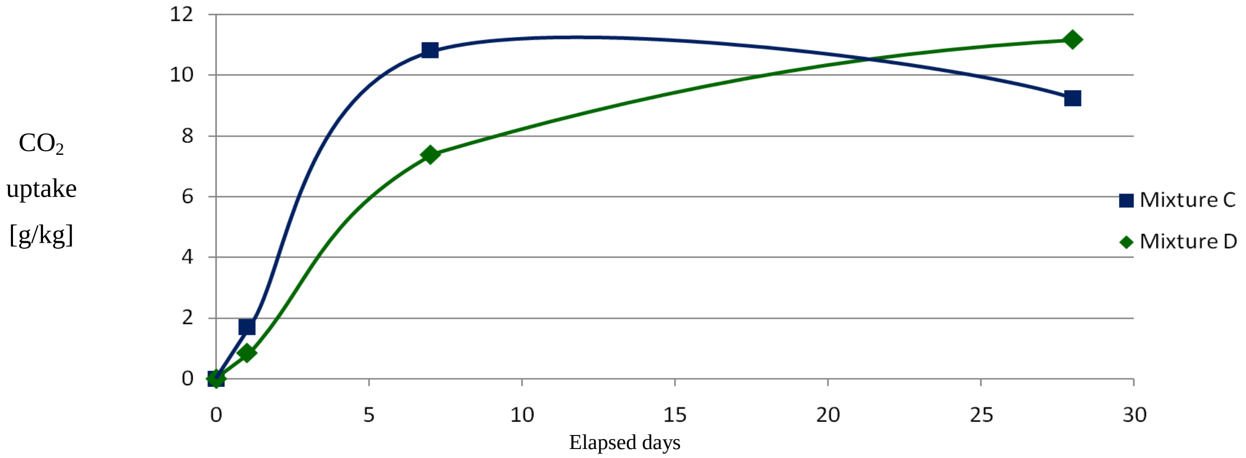

**Figure 4.23**. Pattern of CO$_2$ absorption during the first 28 days of curing for Mixtures C and D.

Additionally, Figure 4.24 illustrates that a faster decline in pressure for each experimental day was reported as for Mixture C, hitting the lowest point (0 bar) both the 7th and 28th days of curing, whilst the pressure of Mixture D mildly decreased, appreciating no more than 0.3 bar.

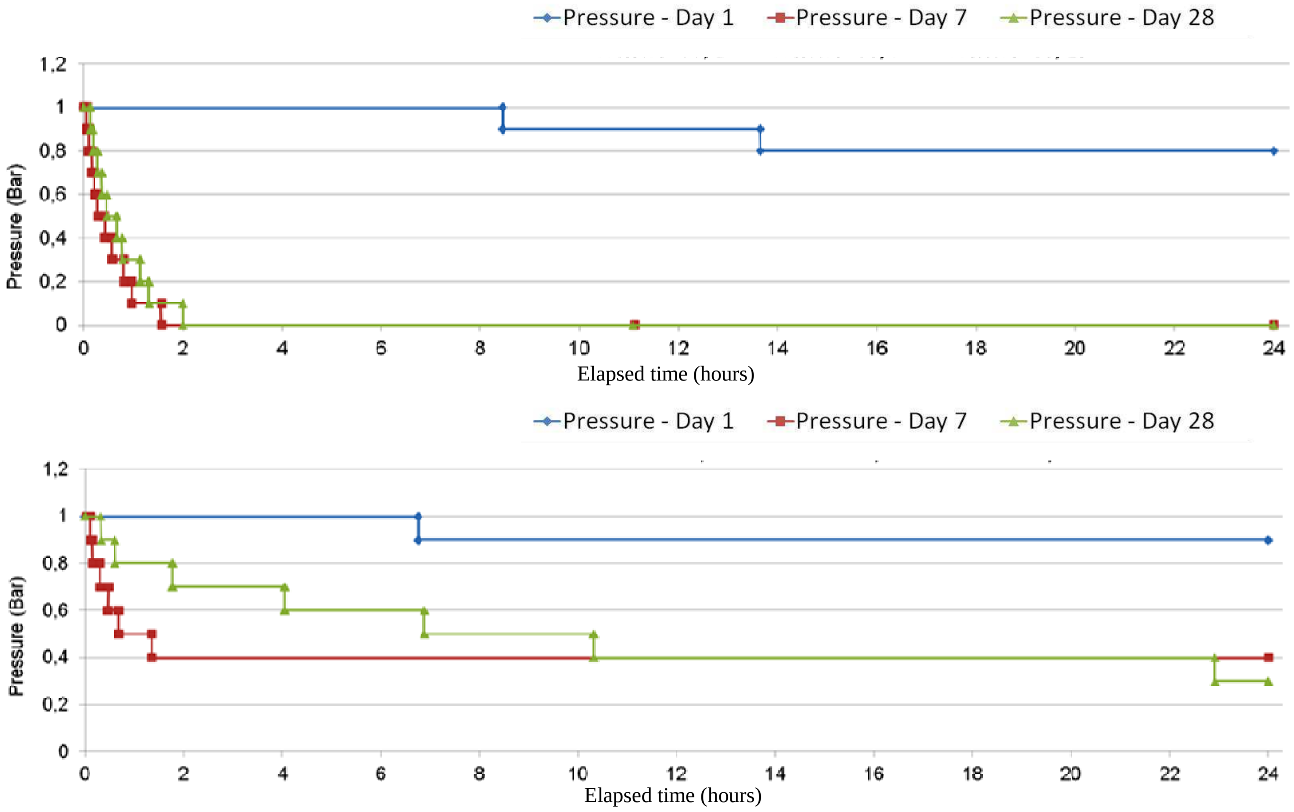

**Figure 4.24**. Pressure variations in time: Mixture C (above) and Mixture D (below).

After having unmoulded, divided into two halves and crushed the samples to powder using a mortar and pestle (Figure 4.25), a post-carbonation XRD and a microscopy analysis on the untreated and treated samples were performed.

**Figure 4.25**. Preparation of the specimens for further analyses.

X-ray diffraction analyses reported in Figure 4.26 and 4.27 demonstrated that although calcite peaks multiplied, portlandite peaks were still detected in the 28th day samples, meaning that there is still room for carbonation.

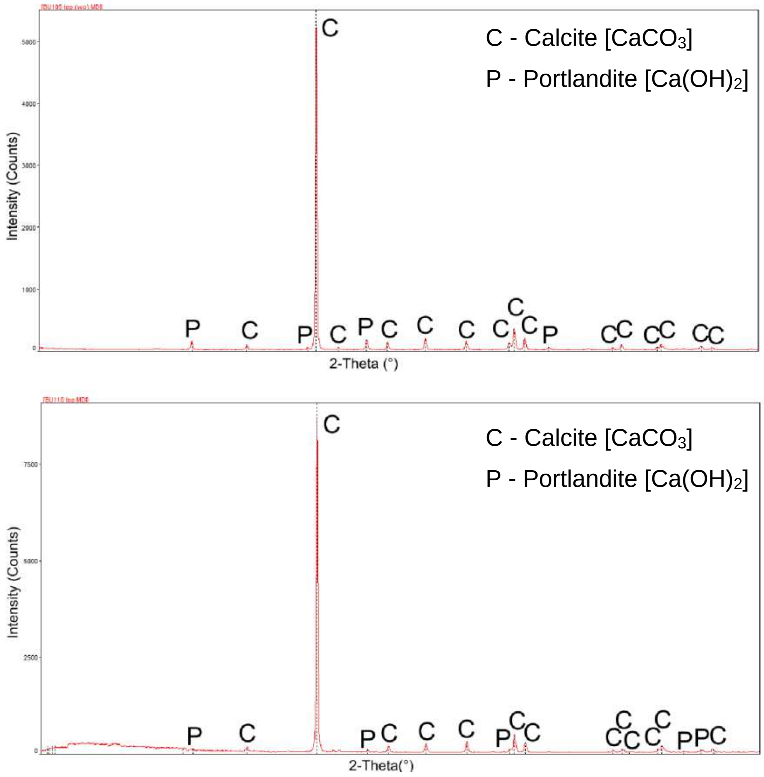

**Figure 4.26.** XRD patterns of untreated (above) and 28th day-treated (below) Mixture C.

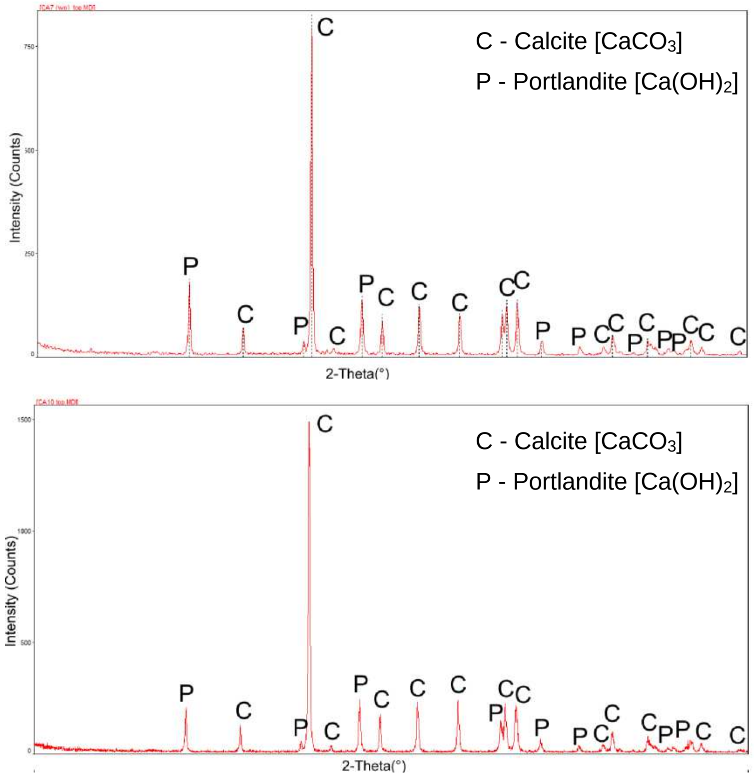

**Figure 4.27.** XRD patterns of untreated (above) and 28th day-treated (below) Mixture D.

Similarly to the analyses conducted on the commercial mortars, several thin sections were prepared for the “ecological mortars”, which were studied by means of a polarizing microscope in transmitted light. Likewise, the pore structure was measured through digital image analysis technique. Also, the porosity of the “ecological mortars” was evaluated according to Computerised Digital Image Analysis, combined with a polarizing microscope in transmitted light.

For both Mixtures C and D, the aggregate composition consisted of calcite fragments. Also, concerning the size range, it was reported a lower grain size in comparison to the commercial mortars previously studied, as a consequence of using lime putty and finely crushed stone fragments from Apuan and Orosei Marble waste in their preparation.

As it can be expected, the following figures underline that carbon uptake occurred in the pores, in which calcite crystals had precipitated. Also, the comparison between the thin sections of untreated and treated samples (Figure 4.28) suggested that, as a consequence of carbonation, a ring structure of calcite was determined, confirming the findings of the studies conducted on the commercial mortars.

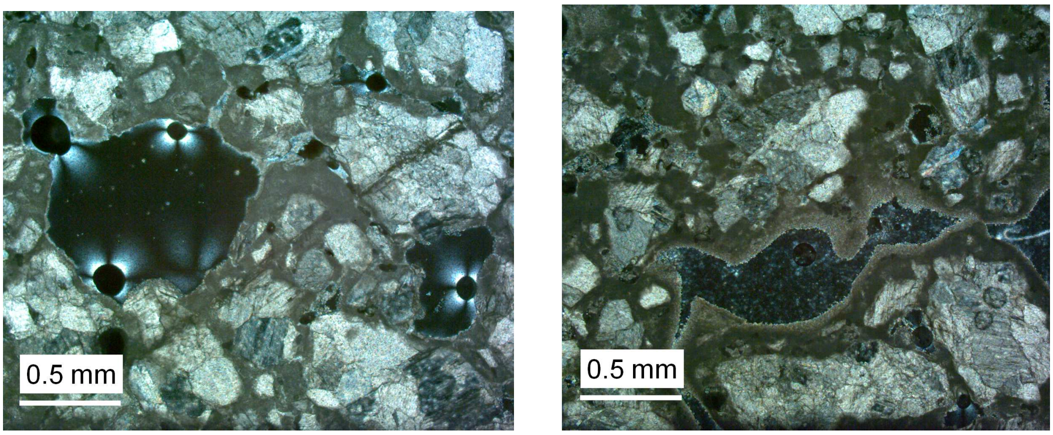

**Figure 4.28.** Comparison between untreated (left) and treated Mixture C (right).

In addition, regarding Mixture D, a decrease from 14% to around 3% was observed in the porosity of the 28th day sample in comparison to the specimen of the first day of curing, due to the presence of calcite along the interior of voids, as a result of calcite precipitation after carbonation (Figure 4.29).

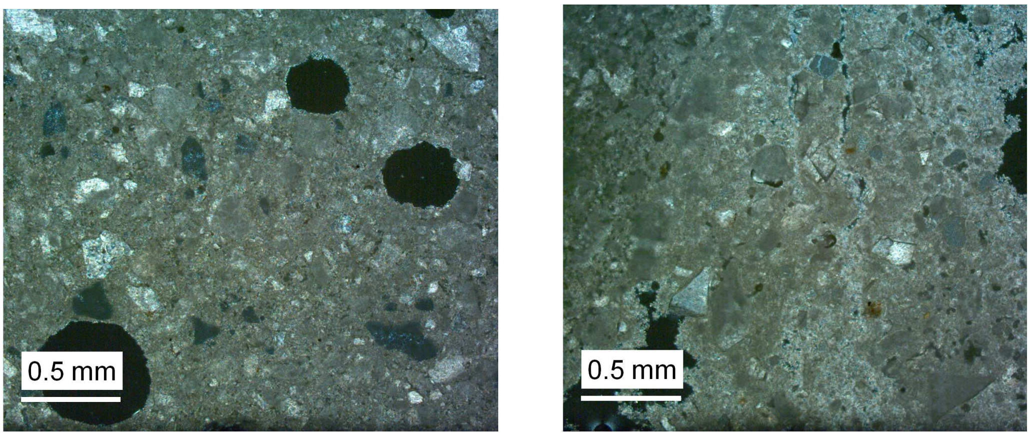

**Figure 4.29.** Some of the several thin sections comparing the 1st day sample (left) with the 28th day sample (right) of Mixture D.

In sum, the total fluctuation in porosity noticed for both Mixtures is reported in Table 4.17 and Figure 4.30.

**Table 4.17.** Porosity figures of of Mixture C (made of Apuan Marble waste) and Mixture D (made of Orosei Marble waste) in the curing period of 28 days.

| | **Porosity [%]** |
|---|---|
| **Mixture C - untreated** | 20 |
| **Mixture C - day 1** | 20 |
| **Mixture C - day 7** | 16 |
| **Mixture C - day 28** | 15 |
| | |
| **Mixture D - untreated** | 14 |
| **Mixture D - day 1** | 11 |
| **Mixture D - day 7** | 6 |
| **Mixture D - day 28** | 3 |

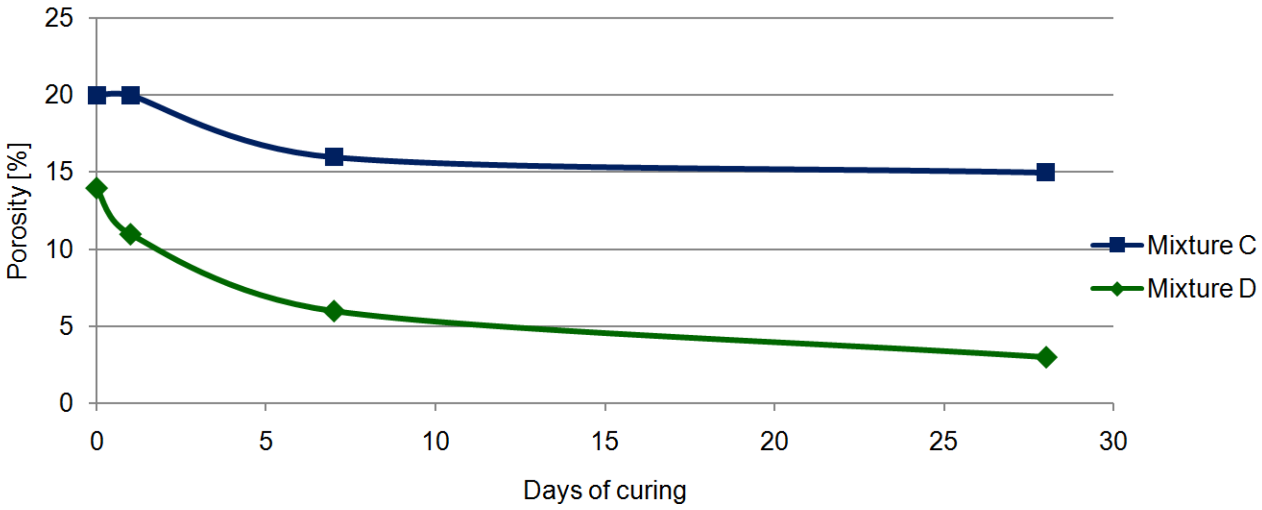

**Figure 4.30.** Observed decrease in the porosity of Mixture C (made of Apuan Marble waste) and Mixture D (made of Orosei Marble waste) in the curing period of 28 days.

The experimental results bore out that the “ecological mortars” are capable to take up $CO_2$, albeit with adsorption values which are somewhat lower than those of the commercial mortars already studied.

Indeed, the commercial mortars analysed consist of a cement mortar and a hydraulic lime, whilst the mortar mixtures manufactured as “ecological mortars” are composed of non-hydraulic lime, that is hydrated lime, and stone waste as sand. Hydrated lime (or lime putty) was chosen as the binder constituent for it is commonly used as external and internal plaster and in rendering due to its ability to give higher breathability to masonry and for it is typically used in the external layer of a plaster, thus in direct contact with air.

Despite the lower $CO_2$ uptake values, whilst the commercial mortars (especially the cement one) after a curing period of 28 days demonstrated the plunge or total disappearance of Portlandite, the “ecological mortars”, both Mixtures C and D, still reported the presence of Portlandite, suggesting that there is room for further carbonation after the 28-day period, hinting at the possibility of a higher percentages of carbon uptake of the “ecological mortars”.

### *4.3 Definition of a carbon uptake index for the “ecological mortars”*

By comparing the $CO_2$ absorption values of the cement and the lime mortars considered in this dissertation, some clear differences were observed. Not only did the cement mortar provide diverse figures of $CO_2$ uptake from the lime mortars during the first 28 days of curing, flattening out quite soon, but this is a distinction that also involves the production of these materials, and in particular their $CO_2$ emissions.

Regarding cement-based and lime-based products, firstly it should be pointed out that carbon emissions in the manufacture of lime are lower than those of cement production. This is due to the fact that during the production process there a significant difference between the heating temperature of cement and lime. In fact, lime is produced at a temperature of around 900°C, whilst cement at about 1400°C. As a consequence, a higher amount of energy is required to produce cement, hence higher $CO_2$ emissions. Additionally, the bulk density of lime is approximately half that of cement, allowing fuel savings, which fluctuate from 20% to 30% (Forum Italiano Calce).

However, the most significant difference between the production of cement-based and lime-based mortars is the quantity of $CO_2$ absorbed from the atmosphere by lime during the setting process. It was estimated that each ton of lime will absorb nearly its own weight of $CO_2$ (Magwood and Feigin, 2014) owing to carbonation. Carbonation allows the carbon dioxide emitted in the production to be reabsorbed, and this is greatest for the pure lime products. Through carbonation, lime plasters can reabsorb up to 90% of the carbon dioxide emitted from the calcination over a 50-year period, whilst cement-based plasters can attain up to 70%. This is due to the fact that the material is less porous and part of the calcium compounds are retained within the siliceous constituents (Berge, 2009). Moreover, although a theoretical reabsorption capacity of 100% could be attained, in practice it is lower, since not every layer of the plaster has an adequate exposure to the atmosphere (Magwood and Feigin, 2014).

Consequently, it is possible to evaluate the quantity of carbon dioxide taken up in the plaster named “Mixture D” during its first 28 days of curing period as a percentage of the $CO_2$ emissions due to the calcinations reaction in the lime manufacture.

According to the European Environment Agency (EEA, 2009), in the lime production the dissociation of limestone produces up to 0.75 tonnes of carbon dioxide per tonne of quicklime, depending on the composition of the limestone and the degree of calcination.

**Table 4.17**. Mix proportions of the Mixture D.

| ID mix | constituents | [g] | % |
|---|---|---|---|
| **D1**<br>**“fine”** | water | 467 | 10.45 |
| | lime putty | 1000 | 22.39 |
| | CC (Orosei marble waste)<br>fine grain size<br>(0 mm – 0.4 mm) | 3000 | 67.16 |
| | *total* | *4467* | *100* |
| **D2**<br>**“medium”** | water | 300 | 6.98 |
| | lime putty | 1000 | 23.26 |
| | CC (Orosei marble waste)<br>fine grain size<br>(0 mm – 0.4 mm) | 1500 | 34.88 |
| | CC (Orosei marble waste)<br>medium grain size<br>(0.8 mm – 1.4 mm) | 1500 | 34.88 |
| | *total* | *4300* | *100* |

**Table 4.18**. Mix proportions of 1 kg of the Mixture D.

| ID mix | constituents | [g] | % |
|---|---|---|---|
| **D1**<br>**“fine”** | water | 104.54 | 10,45 |
| | lime putty | 223.86 | 22.39 |
| | CC (Orosei marble waste)<br>fine grain size<br>(0 mm – 0.4 mm) | 671.59 | 67.16 |
| | *total* | *1000* | *100* |
| **D2**<br>**“medium”** | water | 69.77 | 6.98 |
| | lime putty | 232.56 | 23,26 |
| | CC (Orosei marble waste)<br>fine grain size<br>(0 mm – 0.4 mm) | 348.84 | 34.88 |
| | CC (Orosei marble waste)<br>medium grain size<br>(0.8 mm – 1.4 mm) | 348.84 | 34.88 |
| | *total* | *1000* | *100* |

Taking into account this figure, and remembering the mix proportions of the ecological mortars, in particular Mixture D (Table 4.17), it is possible to assess the percentage of carbon dioxide reabsorbed through carbonation. In Table 4.18 the amount of lime putty in 1 kg of plaster is reported both for the “fine” and the “medium” mixtures.

Given that the experimental plaster that underwent the carbonation tests under mild accelerated conditions consisted of both mixtures, it is possible to consider an average value of 228.21 g of lime putty per kilogram of plaster. Thus, from these data, it can be deduced that in one kilogram of plaster the content of lime putty is 228.21 g, whose production required 171.16 g of $CO_2$, obtained according to the following:

| | |
|---|---|
| → **0.75 t $CO_2$/ t lime** | *tonnes of carbon dioxide produced per tonne of lime* |
| → **750g $CO_2$/ 1kg lime** | *amount of carbon dioxide produced per 1 kg of lime* |
| → **171.16 g $CO_2$/ 228.21 g lime** | *amount of lime contained in 1 kg of plaster (Mixture D)* |

From the comparison between the amount of $CO_2$ due to the calcination and the amount of $CO_2$ reabsorbed during the experimental tests, it was calculated and displayed in Table 4.19 the percentage of carbon dioxide reabsorbed from Mixture D.

**Table 4.19.** Percentage of carbon dioxide reabsorbed from Mixture D.

| | | |
|---|---|---|
| **g of absorbed $CO_2$** [g $CO_2$/1kg of plaster] | day 28 | **11.19** |
| | day 7 | **7.39** |
| | day 1 | **0.85** |

| | | | |
|---|---|---|---|
| **% reabsorbed** | **day 28** | **6.54** | **%** |
| | **day 7** | **4.32** | **%** |
| | **day 1** | **0.50** | **%** |

Therefore, from the calculation it follows that the $CO_2$ absorbed during the first 28 days of the curing period of Mixture D consist of approximately 6.5% of that emitted in the calcination reaction of the lime production.

As a matter of fact, this figure does not represent a negligible percentage of carbon reabsorbed by lime plasters, not to mention the amount which may be absorbed in the remaining service life, as well as after its demolition.

*References*

B. Bary and A. Sellier (2004). Coupled moisture-carbon dioxide-calcium transfer model for carbonation of concrete. Cement and Concrete Research 34, 1859-1872.

B. Berge (2009). The Ecology of Building Materials, Architectural Press, Oxford, UK.

Ciccu R., Mazzella A., Tilocca C. and Mei G. (2011). $CO_2$ uptake and metal release capacity of carbonated Sulcis Coal Ash, Proceedings Sardinia 2011, Thirteenth International Waste Management and Landfill Symposium S. Margherita di Pula, Cagliari, Italy; 3 - 7 October 2011, CISA Publisher, Italy.

J. Elsen (200&). Microscopy of historic mortars - a review, Cement and Concrete Research 36, 1416-1424.

EN 1015-11:1999/A1:2006 - Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar.

EN 998-1:2010 - Specification for mortar for masonry. Rendering and plastering mortar.

European Environment Agency [EEA] (2009). “EMEP/EEA Emission inventory guidebook - 2.A.2 Lime production” - available at: http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009.

Forum Italiano Calce (Italian Lime Forum) - *www.forumcalce.it.*

T. Ishida, K. Maekawa, and M. Soltani (2004). Theoretically identified strong coupling of carbonation rate and thermodynamic moisture states in micropores of concrete. Journal of Advanced Concrete Technology, 2, 213-222.

S. Kashef-Haghighi and S. Ghoshal (2010). $CO_2$ Sequestration in Concrete through Accelerated Carbonation Curing in a Flow-through Reactor, Industrial & Engineering Chemistry Research, 49 (3), 1143–1149.

C. Magwood and J. Feigin (2014). “Making Better Buildings: A Comparative Guide to Sustainable Construction for Homeowners and Contractors”, New Society Publishers, Canada.

M.J. Mavor (1990). Measurement and evaluation of coal sorption isotherm data. In: “Society of Petroleoum Engineers, Annual Technical Conference and Exhibition”, 23-26 September 1990, New Orleans, Louisiana, SPE Paper 20728, 157-170.

A. Mazzella (2011). “Studio preliminare per la valutazione della fattibilità di un progetto di CO2-ECBM nel bacino carbonifero del Sulcis”, thesis of the Geoengineering and Environmental Technologies Ph.D., University of Cagliari, Cagliari.

A. Mazzella, C. Tilocca, R. Ciccu, and G. Mei (2012). Capacità di assorbimento della CO2 e di rilascio dei metalli pesanti delle fli-ash del carbone "Sulcis", Resoconti della Associazione Mineraria Sarda Iglesias, Anno CXIV-CXVII 2009-2012.

V. G. Papadakis,, C. G.Vayenas, and M. N. Fardis (1991). Physical and chemical characteristics affecting the durability of concrete. ACI Materials Journal, 88(2), 186-196.

International Union of Laboratories and Experts in Constructions Materials, Systems and Structures [RILEM] (1988). CPC-18 measurement of hardened concrete carbonation depth.

International Union of Laboratories and Experts in Constructions Materials, Systems and Structures [RILEM] (2004). “Porosity of Mortars”, edited by M. Thomson, J-E. Lindqvist, J. Elsen and C. J. W. P. Groot, in “Report 28: Characterisation of Old Mortars with Respect to their Repair”. RILEM TC 167-COM: State-of-the-Art Report, edited by C. Groot, G. Ashall, J. Hughes, 75-104, RILEM Publications, Bagneux, France.

O.L. Shtepenko, C.D. Hills, N.J. Coleman and A. Brough (2005). Characterization and Preliminary Assessment of a Sorbent Produced by Accelerated Mineral Carbonation, Environmental Science & Technology 39, 345-354.

G. Soave (1972). Equilibrium constants from a modified Redlich-Kwong equation of state, Chemical Engineering Science, 27, 1197-1203.

H. Song and S. Kwon (2007). Permeability characteristics of carbonated concrete considering capillary pore structure, Cement and Concrete Research 37, 909–915.

H.H. Steinour (1959). Some effects of carbon dioxide on mortars and concrete-discussion, Journal of the American Concrete Institute I 30, 905-907.

# Chapter 5. Economic Feasibility

In this chapter the economic feasibility of producing Mixture D as the final layer of a plaster will be discussed.

From a study performed on the global raw production of dimension stones, it was argued that usually the production of raw quarrying waste is approximately 51% of total volume extracted, as reported in Table 5.1 (Montani, 2011; USGS, 2011; United Nations Commodity Trade Statistics Database, 2012).

**Table 5.1.** World production of dimension stones

| World production of dimension stones | | | |
|---|---|---|---|
| | **Gross quarrying** | **Quarrying waste** | **%** |
| 2003 | 57000 | 29222 | 51.27 |
| 2004 | 61650 | 31557 | 51.19 |
| 2005 | 64750 | 33176 | 51.24 |
| 2006 | 70450 | 36098 | 51.24 |
| 2007 | 78500 | 40167 | 51.17 |
| 2008 | 79600 | 40711 | 51.14 |
| 2009 | 79150 | 40446 | 51.10 |
| 2010 | 84450 | 43161 | 51.11 |

Taking into consideration this figure, a calculation of the possible annual revenue from selling the CC fraction of the Orosei Marble waste was performed, as displayed in Table 5.2. A overall revenue of 1,836,000 million USD was obtained, provided that all waste is sold.

**Table 5.2.** Calculation of the possible annual revenue from Orosei Marble Waste.

| **Annual Orosei gross quarrying production*** [mc] | **Annual waste output available for sale (51%)** [mc] | **volumetric mass density** [t/mc] | **Annual waste output available for sale** [t] | **Average Unit Value (FOB)**** [USD/t] | **Average Unit Value (FOB)**** [USD/kg] | **Possible Annual Revenue** [USD] |
|---|---|---|---|---|---|---|
| 300,000 | 153,000 | 1.50 | 229,500 | 8.00 | 0.008 | 1,836,000 |

*Source: Careddu et al., 2010.
**FOB - Freight On Board.

Also, from a market analysis of market prices of hydrated lime, which is usually sold in 25 kg plastic bags, the average value for one kilogram of material was deduced and reported in Table 5.3.

**Table 5.3.** Calculation of the average value of hydrated lime.

| **Average Value for one 25 kg plastic bag**<br>[USD] | **Average Value for 1 kg of material**<br>[USD/kg] |
|---|---|
| 17.85 | 0.714 |

An estimate of the costs of producing recycled aggregates from Orosei Marble waste was needed at this point, and it was provided according to U.S. Geological Survey, 1998 (USGS, 1998).

In Table 5.4 the different parameters considered to be necessary in a recycling facility are listed. Since the costs are subdivided into capital and operating costs, an initial period in which a new private investment is required was considered.

**Table 5.4.** Estimated costs of producing recycled aggregates from Orosei Marble waste.

| **Capital Costs** | **Mean Price [U.S. Dollar/ton]** |
|---|---|
| equipment | 4.52 |
| labour costs | 0.25 |
| *Total Capital Costs* | 4.77 |
| **Operating Costs** | |
| equipment maintenance | 0.72 |
| labour costs | 0.70 |
| supplies | 0.03 |
| fuel | 0.19 |
| recovery of capital | 0.64 |
| fixed costs | 0.90 |
| *Total Operating Costs* | 3.18 |
| **Total (Capital Costs + Operating Costs)** | **7.95** |
| **Revenues** | |
| Average product price | 8.00 |

*Assumed cash flow period: 11 years*

During this initial period, the overall costs are the sum of capital and operating costs, and the profit is calculated as follows:

Profit = Revenues - Total costs = 0.05 U.S. Dollar/ton = 0.00005 U.S. Dollar/kg

Afterwards, the operating costs were considered as the only necessary investment for the following years, allowing for the calculation:

Profit = Revenues - Total costs = 4.82 U.S. Dollar/ton = 0.00482 U.S. Dollar/kg

In light of this, two likely scenarios were allowed for in order to make a correct calculation of costs:

- Case 1: initial period (Production costs: Capital Costs + Operating Costs).

Initially, it was calculated that, according to the mix proportions of the mixture D mentioned in Chapter 4 of this dissertation, a typical commercial bag of 25 kg of mixture D, made up of 25% lime putty and 75% Orosei Marble waste, should contain about 18.75 kg of recycled aggregates from Orosei Marble waste. It follows that, since the estimated cost of producing recycled aggregates is 7.95 U.S. Dollar/ton or 0.00795 U.S. Dollar/kg (as calculated in Table 5.4), a simple multiplication gives the result of 0.15 USD as the cost of the amount of recycled aggregates from Orosei Marble waste in a commercial bag of 25 kg (Table 5.5).

**Table 5.5.** Cost of the amount of recycled aggregates from Orosei Marble waste in a commercial bag of 25kg (scenario 1).

| Amount of recycled aggregates from Orosei Marble waste in a commercial bag of 25kg | | Estimated costs of producing recycled aggregates [U.S. Dollar/kg] | | |
|---|---|---|---|---|
| 18.75 kg | X | 0.00795 USD | = | 0.15 USD |

Afterwards, the calculation of the costs from the purchase of hydrated lime was taken into consideration. From Table 5.3, it is possible to notice that the average value of 1 kg of hydrated lime is 0.714 U.S. Dollar/kg, which multiplied by the amount of lime estimated to be in a commercial bag of 25 kg of mixture D (25% or 6.25 kg) will give an overall cost of 4.46 U.S. Dollar.

Then, by considering that both hydrated lime and mixture D can be used as plasters, it was calculated the profit obtained from the sale of a commercial bag of 25 kg of mixture D as compared to the sale of a typical commercial bag of 25 kg of hydrated lime.

As reported in Table 5.3, the price of a typical commercial bag of 25 kg of hydrated lime was estimated at 17.85 U.S. Dollar.

On consideration of total costs, namely the cost from the purchase of hydrated lime and the cost of the production of aggregates from Orosei Marble waste, an overall cost of 4.61 U.S. Dollar was estimated for the production of one bag of mixture D. Consequently, supposing that the price of a commercial bag of 25 kg of mixture D is the same of a commercial bag of 25 kg of hydrated lime, the estimated net profit from the sale of a bag of mixture D amounted to 13.24 U.S. Dollar, as reported in Table 5.6.

**Table 5.6.** Estimated net profit from the sale of a commercial bag of 25 kg of mixture D (scenario 1).

| **Mixture D** | **Amount** [kg] | **Costs** [USD] | **NET PROFIT** [USD/25kg] |
|---|---|---|---|
| lime putty (25%) | 6.25 | 4.46 | 17.85 - 4.61<br>**=13.24** |
| Orosei Marble waste (75%) | 18.75 | 0.15 | |
| **Total** | **25.00** | **4.61** | |

- Case 2: period at operating production (Production costs: Operating Costs).

As far as the second scenario is concerned, the costs of the production of aggregates from Orosei Marble waste are related to operating costs only. In other words, whilst in the first case study total costs were calculated as reported in Table 5.4 as follows:

4.77 (capital costs) + 3.18 (operating costs) = 7.95 U.S. Dollar/ton;

In the second case study, total costs are related to operating costs of the recycling facility, amounting to 3.18 U.S. Dollar/ton only.

As a consequence, the estimated costs of producing recycled aggregates are slightly lower than in the first case, standing at 0.06 U.S. Dollar/25 kg bag (Table 5.7).

**Table 5.7.** Cost of the amount of recycled aggregates from Orosei Marble waste in a commercial bag of 25kg (scenario 2).

| **Amount of recycled aggregates from Orosei Marble waste in a commercial bag of 25kg** | | **Estimated costs of producing recycled aggregates [U.S. Dollar/kg]** | | |
|---|---|---|---|---|
| 18.75 kg | X | 0.00318 USD | = | 0.06 USD |

By repeating the same procedure, an evaluation of the net profit from the sale of a bag of mixture D was undertaken also for the second case study and shown in Table 5.8

**Table 5.8.** Estimated net profit from the sale of a commercial bag of 25 kg of mixture D (scenario 2).

| **Mixture D** | **Amount** [kg] | **Costs** [USD] | **NET PROFIT** [USD/25kg] |
|---|---|---|---|
| lime putty (25%) | 6.25 | 4.46 | 17.85 - 4.52<br>**=13.33** |
| Orosei Marble waste (75%) | 18.75 | 0.06 | |
| **Total** | **25.00** | **4.52** | |

From the comparison between the two scenarios analysed, in can be pointed out that there is a marginal difference from the net profits. In fact, the most affecting factor is the cost of the amount of hydrated lime necessary for the manufacture of mixture D, which is the same in both scenarios.

Further important considerations can be taken into account. At the beginning of this dissertation, it was mentioned that the production of aggregates is somewhat unprofitable for quarrying companies of dimension stone, since aggregates are mainly aimed at the local market, while dimension stones have a global market and market prices for aggregates are much lower than those for dimension stones. Therefore, it was drawn a comparison between the possible profit from the sale of Orosei Marble waste as either aggregates or utilising it for the manufacture of mortars such as mixture D. The assessment was undertaken for both scenarios previously considered, and reported in the following tables (Tables 5.9 and 5.10).

**Table 5.9.** Scenario 1: estimated net profit from the sale of aggregates (left) and the sale of mixture D (right).

| **(Production costs: Capital Costs + Operating Costs)** | | | |
|---|---|---|---|
| **Production of recycled aggregates from Orosei Marble waste** | **[USD/kg]** | **Revenues [USD/kg]** | **NET PROFIT** |
| **Capital Costs [USD/kg]** | 0.00477 | 0.008 | 0.008 - 0.00795= **0.00005 [USD/kg]** |
| **Operating Costs [USD/kg]** | 0.00318 | | |
| **Total [USD/kg]** | 0.00795 | | |

| **(Production costs: Capital Costs + Operating Costs)** | | | |
|---|---|---|---|
| | **Amount [kg]** | **Costs [USD]** | **NET PROFIT** |
| **lime putty 25%** | 6.25 | 4.46 | 17.85 - 4.61= 13.24 [USD/25kg] |
| **Orosei Marble waste 75%** | 18.75 | 0.15* | 13.24/25kg= **0.529 [USD/kg]** |
| **Total** | 25.00 | 4.61 | |

**Table 5.9.** Scenario 2: estimated net profit from the sale of aggregates (left) and the sale of mixture D (right).

| **(Production costs: Operating Costs)** | | | |
|---|---|---|---|
| **Production of recycled aggregates from Orosei Marble waste** | **[USD/kg]** | **Revenues [USD/kg]** | **NET PROFIT** |
| **Operating Costs [USD/kg]** | 0.00318 | 0.008 | 0.008 - 0.00318= **0.00482 [USD/kg]** |
| **Total [USD/kg]** | 0.00318 | | |

| **(Production costs: Operating Costs)** | | | |
|---|---|---|---|
| | **Amount [kg]** | **Costs [USD]** | **NET PROFIT** |
| **lime putty 25%** | 6.25 | 4.46 | 17.85 - 4.52= 13.33 [USD/25kg] |
| **Orosei Marble waste 75%** | 18.75 | 0.06 | 13.33/25kg= **0.533 [USD/kg]** |
| **Total** | 25.00 | 4.52 | |

From the data, it can be confirmed that the production of aggregates is significantly less profitable than the manufacture of other by-products from natural stone waste such as mortars and plasters. Moreover, the two prospected scenarios provided a fractional difference in terms of net profits, especially as far as the production and sale of mixture D are concerned, whilst there is a considerable decrease in profits in consideration of the manufacture and sale of recycled aggregates.

## *References*

N. Careddu, G. Siotto, and A. Tuveri (2010). Evolution of a marble quarry: from open cast to underground exploitation. Proc. Global Stone Congress, Alicante, ESP, 2010.

C. Montani (2011). “XXII Report 2011 world marble and stones”, Aldus Casa di Edizioni, Carrara.

United Nations Commodity Trade Statistics Database, available at: http://comtrade.un.org/db/default.aspx.

United Nations Environment Programme's [UNEP] (1999). “Global Environment Outlook (GEO) 2000”, UNEP Nairobi.

US Department of the Interior, United States Geological Survey [USGS], (1998). U.S. GEOLOGICAL SURVEY CIRCULAR 1176, edited by D. R. Wilburn and T. G. Goonan. “Aggregates from Natural and Recycled Sources. Economic Assessments for Construction Applications - A Materials Flow Analysis”, Central Region, Denver, Colorado - available at: http://greenwood.cr.usgs.gov/pub/circulars/c1176/c1176.html.

US Department of the Interior, United States Geological Survey [USGS] (2011). “Mineral Commodity-Summaries 2011”. Reston, Virginia, ISBN 978-1-4113-3083-2.

# Conclusion

This study, focused on the re-use of quarrying waste, pointed out that not only could coping with waste be environmentally damaging, but it is also economically expensive for the stone industry, which in addition has to deal with the economic loss caused by the lower efficiency of quarrying.

The experimental work took into consideration three waste typologies supplied by a quarry of the Orosei Marble District. According to the characterisation, each of the three typologies mainly consists of **calcium carbonate.**

The absence of pollutants (hazardous elements, alkali and heavy metals) was highlighted in order to show that their use is suitable for **commercial purposes.** It follows that the waste taken into consideration may have a **potential economic value** and may be re-used for the production of mortars, called **"ecological mortars"** for their environmental-added value.

It was chosen to further enhance the environmental advantages of re-using stone waste for the production of mortars by investigating the **$CO_2$ uptake** of the "ecological mortars", since a percentage of $CO_2$ emissions from the production of mortars is reabsorbed as the it hardens, owing to **carbonation**.

Firstly, an assessment of the $CO_2$ uptake of some common **commercial mortars** through some experimental tests was undertaken, in order to study their characteristics and establish both a test methodology and a set of parameters to which compare, afterwards, the performance of the "ecological mortars".

The experimental results showed that the commercial mortars are capable to take up $CO_2$, and in particular:

- the **cement mortar** showed higher uptake figures, although after the first 28-day period they levelled off. This was confirmed by the disappearance of Portlandite in the XRD analysis;
- the hydraulic lime reported lower uptake values, albeit on the increase.

Several mixtures were afterwards prepared by utilising different fractions of the Orosei Marble waste previously characterised. Also, an additional mixture were made by adding crushed stone waste from the famous Apuan Marbles, so as to compare its performance to that of the "ecological mortars".

To sum up, it was demonstrated that the **"ecological mortars"** are capable to take up $CO_2$, as well, even though lower uptake figures as compared to the commercial mortars were reported. In particular:

- the **mixture C (characterised by Apuan Marbles)** showed a fall in the carbon absorption after the 7th day of curing;
- the **mixture D (made up of Orosei Marbles)** reported an increasing uptake, also confirmed by the calcimetry analysis.

Despite the lower uptake figures, the behaviour of mixture D suggests that there is room for further carbonation after the first 28-day period, thus the chance of **higher uptake considering a longer curing period**.

Even though it can be argued that these figures could be fairly low, they represent a **significant amount** considering the period of service life and during the demolition of mortars and plasters. Indeed, it is a period that lasts for decades during which mortars continue to take up carbon dioxide from the air, albeit with a slower pace.

From the economic standpoint, according to the comparison between the estimated profit from the sale of either aggregates or mortars (Mixture D), it can be deduced that the **production of mortars is evidently more profitable**, although an initial investment with a cash flow period is required.

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# Featured Publications

Furcas C., Balletto G., Naitza S., and Mazzella A. (2014). "Evaluation of $CO_2$ Uptake under Mild Accelerated Carbonation Conditions in Cement-Based and Lime-Based Mortars", *Advanced Materials Research* 980, 57-61-ISSN: 1022-6680; DOI: 10.4028/www.scientific.net/AMR.980.57.

Furcas C., Balletto G. (2014). "Increasing the value of dimension stone waste for a more achievable sustainability in the management of non-renewable resources*", Journal of Solid Waste Technology and Management* 40(3), 185-196-ISSN 1088-1697; DOI: 10.5276/JSWTM.2014.185.

Furcas C., Balletto G. (2013). "Coping with the extraction of dimension stones. Current situation and sustainable outlook for natural stone waste management". *Mineral Resources and Mine Development*, Martens P.N. (ed.), Verlag Gluckauf GmbH, Essen, 219-233-ISBN 978-3-86797-154-6.

Furcas C., Balletto G. (2013). *Converting waste from the dimension stone industry into sustainable environmental resources. Current trends, market opportunities and future outlooks*, Proceedings of The 28th International Conference on Solid Waste Technology and Management - ICSW 2013, 10 – 13 March, Philadelphia, USA, 104-115-ISSN: 1091–8043.

Furcas C., Balletto G. (2012). *Enhancing Environmental Sustainability In The Building Industry: The Re-Use Of Natural Stone Waste*, Proceedings of the 13TH International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production - SWEMP 2012, 28 – 30 November, New Delhi, India, 104-115-ISSN: 2167–3365.