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Sustainability and environmental impact of the Italian ceramic tile industry

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Abstract

The increasing consumption rates among citizens and the uncontrolled exploitation of natural resources have made environmental pollution and management of waste the main problems facing humanity in its upcoming future. Together with generation of energy and transport, industrial production certainly plays a key role in the genesis of these problems. It is for this reason that the concepts of environmental, social and economic sustainability have emerged over the years as the cornerstones for future development. In light of this, the most forward-looking industries have begun to study their impact on environment and society in order to improve their performances and, at the same time, to anticipate the increasingly rigorous environmental regulations.

In this work, various performance indicators related to the Italian ceramic tile sector will be presented and discussed. In particular, the emission factor of characteristic pollutants will be reported on a period of up to fifteen years while data regarding waste management, concentration of pollutants and emission legal limits for the last decade will be here disclosed as a result of a vast analysis on recorded data.

The collected information describes the present level of performance of the ceramic tile manufacturing industries in Italy and shows how recycling is now a consolidated reality and how some pollutants, such as particulate matter, fluorine and lead are actually disappearing from production processes and how others, such as volatile organic compounds, are increasing instead. Moreover, the adoption of alternative raw materials for the production of ceramic tiles is discussed and the implementation of the recycling of various waste is addressed at experimental or industrial scale. Finally, the development of a new ceramic engobe with high content of waste glass (20%) is presented as an experimental example of reutilization of resources in the ceramic tile industry.

CONTENTS

Introduction

The present thesis project, in the framework of the PhD course in Civil, Chemical, Environmental and Materials Engineering of the University of Bologna, has been funded by *Regione Emilia Romagna* in the context of *POR FSE 2014/2020 Obiettivo tematico 10*. The research activity has been mainly developed at *Centro Ceramico* (www.centroceramico.it), a research center internationally recognized for its competencies in research on ceramic materials and tests for the ceramic industry.

This research project focuses on the sustainability and the environmental impact of the Italian ceramic tile industry, which is in its greatest part represented by factories located in the Emilia-Romagna region of the Italian peninsula, in particular in the *Sassuolo* district. Although still suffering due to the significant market crisis that hit the construction industry after 2007-2008, the ceramic tile industry stands as a leading sector of the regional economy, actually representing one of the most successful examples of *Made in Italy* production recognized and appreciated worldwide.
As a consequence of the deep-rooted history of Italian ceramics and the great expertise of ceramic manufacturers, this industrial sector has always experienced a constant technological innovation which granted a continuous expansion and paved the way for future developments. Further, since the 1970s, Italy has been the leading country for innovation in both ceramic products and process technology, and this has been recently confirmed with the arrival on the market of large ceramic slabs (up to 120x240, 160x320 cm) and tiles of variable thicknesses (in the range from 3 to 30 mm) and with the introduction of digital printing as the main decoration technology for ceramics. However, unlike the past where technological innovations meant a competitive advantage lasting at least a decade, nowadays the fast automation and replicability of processes means that innovations are quickly spread across the world, flattening the market and rendering the results of innovations year after year more limited. On the other hand, the high concentration of industrial installations raised the problem of the

environmental pollution. The high number of sources for acoustic, water, soil and air pollution represented by factories, has brought about new responsibilities for industry, which shall no longer only pursue the economic factor, but also avoid overburdening the environment and society. In fact, with the introduction of the concepts of sustainability, it has been recognized that economic realities are actually embedded within a broad ecosystem that also includes the environment and people, and that in order to sustain itself over time, industrial production must be able to equally consider all the constituents of the system and not pursue profit alone.

It is mainly for these reasons that the Italian ceramic tile industry is facing now new problematics, embracing the sustainability of the production processes and its perceived legitimacy, and not simply related to the continuous development and expansion of the industrial sector. In this light, ceramic tile manufacturers shall direct future efforts towards meeting environmental, economic and social obligations at the same time, pursuing sustainability and constant technological progress as the main drivers of development.

Actually, the ceramic sector in Emilia-Romagna, in its industrial representation by the association of ceramic manufacturers *Confindustria Ceramica* and in its cooperation with regional institutions, has been involved since years in the annual assessment of the industrial performance, especially concerning atmospheric emissions, energy expenditure and materials recycling rates. Thanks to the annual updating of the environmental report known as *Rapporto Integrato*, which integrally addresses since 1998 a whole series of key indicators regarding the impact of the industrial production, the ceramic tile sector has been able to take record along the years of its performance, thus succeeding in aiming for a continuous improvement.

In particular, through the constant monitoring and study of production processes, it was possible to take action to reduce the emissions of some characteristics pollutants of the ceramic tile sector, as the particulate matter and fluorine compounds, now largely below the most rigorous limits adopted at European level. Eventually, some pollutants, as lead (Pb), have been completely eliminated from industrial processes, as a consequence of the complete revolution in the nature of raw materials and resources involved. On the other side, it was also possible to spot new pollutants related to the most recently introduced technological innovations. This is the case for volatile organic compounds and aldehydes, which have been increasing during the last decades, and for the most part related to the digital decoration process. Regarding recycling practices, this industrial sector has always been leader in the circular economy of materials, being able to entirely reutilize both resources and waste generated or to grant them an alternative utilization perspective in other industrial sectors.

During the present research project, the updating of the key performance indicators for the ceramic tile industry has been determined for the last three years, highlighting the evolution trends in the emission of characteristic pollutants and in the recycling of resources. The pollutants considered were particulate matter, fluorine compounds, lead, volatile organic compounds, aldehydes, carbon dioxide and nitrogen and sulfur oxides, while the recycling percentages of water and solid waste within factories were considered as performance indicators for recycling practices.

All data that have been used for the assessments have been collected by the Emilia-Romagna region directly from ceramic tile producers and delivered to *Centro Ceramico* for research purposes according to the cooperation agreement between the research center *Centro Ceramico*, *Confindustria Ceramica* and Emilia-Romagna Region.

Besides the mentioned updating, the data were used to obtain further performance indicators in order to broaden the discussion on recycling and waste management practices. In particular, the new indicators here presented are the actual water consume and demand within factories, the total amount of solid waste produced, focusing mainly on unfired and fired scrap, exhausted lime and ceramic sludges coming from the industrial production processes, the amount of solid waste and water recycled inside the ceramic body and the relative percentage of internal or external recycling, as well as of landfilling of waste. Data was also utilized for a study on the positioning of the emission levels and legal limits from singular factories in relation to the currently enforced emission thresholds associated with the best available techniques at European level. Alongside the exposition of data, the different trends and progressions of the performance indicators were inspected and discussed in order to identify the most impacting process steps and weak points of the entire production system, starting with the choice of raw materials and ending with the recycling of waste.

Consistent with the discussion on recycling practices, an experimental work on the development of a ceramic engobe with a high content of waste glass is also presented. Starting from a commercial engobe, its formulation was modified by replacing the portion of a zircon-rich frit with two sources of waste glass in order to reduce the use of expensive, non-renewable raw materials and, at the same time, to prevent the landfilling of glass by promoting its recycling. This research activity has been carried out in collaboration with the Department of Materials and Ceramic Engineering at the University of Aveiro, under the supervision of Prof. Maria Paula Seabra during a six months exchange period.

In the framework of this PhD, I have been also involved in the development of a new test method for tile testing. In particular, some research work has been carried out towards the development of a new method to measure tile scratch resistance, as a more controlled alternative to the classic Mohs hardness test. This activity is reported in Annex 1 as it is not strictly related to the main topic of the thesis, even if it shares with it the fundamental ambition of sustainable development, in this case by improving the reliability of quality control procedures.

This compendium of the environmental performance of the Italian ceramic tile industry can help manufacturers target specific actions to address issues which would be otherwise difficult to perceive. For example, the progressive introduction on the market of original decoration patterns or new dimensions of ceramic tiles or, further, the adoption of different raw materials, can lead through time to the increasing progression of specific pollutants which, without any record, would be hard to correlate with the introduced innovations. At the same time, it can happen that certain recently adopted market or environmental policies concerning pollution control or recycling practices have a positive effect on the sustainability of the production processes, encouraging manufacturers and policy makers to find agreements in order to continue further down the same path with mutual benefits. In addition, the presented data can also be useful for the updating of environmental regulations and revision of quality standards, providing a reliable database and avoiding, though, the risk of introducing emission limits and performance requirements that are then too rigorous or, on the contrary, too tolerant.

Last but not least, the faithful description of the environmental impact, as realized in the present work, can be a method to certify the attention to environmental protection casted by ceramic tile manufacturers and to ensure transparency in this industrial sector. It is through a transparent and fair behavior towards consumers that the public grant legitimacy to the most virtuous companies and industrial sectors. In fact, compliance with the principles of sustainability and transparency of information are issues that consumers are increasingly concerned about and which, it seems, will play an increasingly important role in directing the future demand for goods and services. Having a long and proven track record in dealing with such questions is a key factor in demonstrating that attention to sustainability is not just a passing craze, but rather a deep-rooted tradition.

Before diving into the data and discussion of the actual level of environmental performance exhibited by the Italian ceramic tile sector, a detailed description of the raw materials and the production processes related to this industrial sector was proposed as very important background information. Likewise, the main concepts of sustainability, the three pillars of sustainable development and, eventually, what does sustainable development actually mean and what does it imply, were treated accordingly to the main purpose of this work.

As previously said, all the research activities related with the assessment of the environmental impact of ceramic tile factories contained in the present PhD project have been carried out at *Centro Ceramico*. During the three-year duration of the project, I have been regularly involved in campaigns to collect environmental samples from ceramic companies, analyzing and elaborating chemical data in order to make them available for further statistical analysis, thus contributing first-hand to the large amount of data here presented and discussed.

1. Ceramic tiles

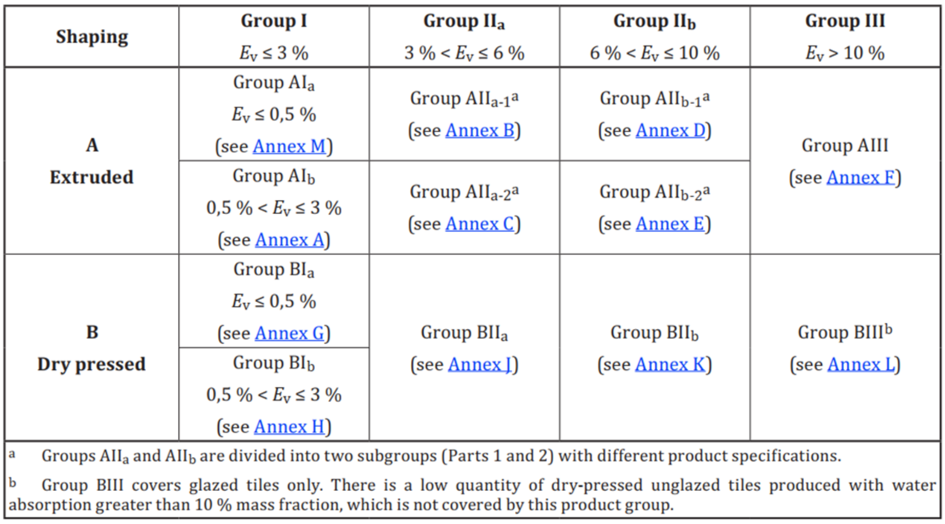
Ceramic is an inorganic and non-metallic material fabricated upon shaping and consolidated by firing at high temperatures. It is employed mostly as a building material under the form of wall, floor and roof tiles or in mosaics, because of its physical and chemical resilience and its safeness in both the use and disposal. Due to the low production costs, the high toughness, the biocompatibility and its peculiar beauty, ceramic is also the constituent of various objects of common use as tableware, sanitaryware, dental or articular prosthesis and artistic crafts.

Italian ceramic has always been one of the famous and most estimated products in the global market of high value commodities. Once with artistic purposes, ceramic is today employed primarily in the building sector all over the world as floor and wall covering. The large widespread of this material is related to its excellent technical and aesthetic characteristics: a high physical and chemical resilience, the high durability and the particular elegance and beauty.

Ceramic tiles can be characterized by different dimensions and thicknesses and can be glazed or unglazed. In the first case, the ceramic body of the tile is covered by a more or less thick layer of glaze, which is a vitreous material compacted to the ceramic mass through firing, with the aim of decorate the tile or to make it waterproof. Unglazed tiles, on the other hand, present a uniform composition.

Ceramic tiles are produced using a heat-treated mixture of natural raw materials as clays, sands and other rocks. The different nature and ratio of these naturally occurring ingredients gives birth to an incredibly wide range of products as, for example, *majolica*, *cottoforte*, *monoporosa*, *stoneware*, *klinker* and *porcelain stoneware*. This last one has become over the last thirty years the most technologically advanced product of the entire ceramic tile sector in Italy. In **Table 1-1** is reported from standard ISO 13006 the classification of ceramic tiles according to the shaping method and the water absorption values.

Table 1-1. Classification of ceramic tiles with respect to water absorption (E_v) and shaping, according to ISO 13006, 2018.



Shaping	**Group I** $E_v \leq 3$ %	**Group II$_a$** 3 % < $E_v \leq 6$ %	**Group II$_b$** 6 % < $E_v \leq 10$ %	**Group III** $E_v > 10$ %
A **Extruded**	Group AI$_a$ $E_v \leq 0{,}5$ % (see Annex M)	Group AII$_{a\text{-}1}$[a] (see Annex B)	Group AII$_{b\text{-}1}$[a] (see Annex D)	Group AIII (see Annex F)
	Group AI$_b$ 0,5 % < $E_v \leq 3$ % (see Annex A)	Group AII$_{a\text{-}2}$[a] (see Annex C)	Group AII$_{b\text{-}2}$[a] (see Annex E)	
B **Dry pressed**	Group BI$_a$ $E_v \leq 0{,}5$ % (see Annex G)	Group BII$_a$ (see Annex J)	Group BII$_b$ (see Annex K)	Group BIII[b] (see Annex L)
	Group BI$_b$ 0,5 % < $E_v \leq 3$ % (see Annex H)			

[a] Groups AII$_a$ and AII$_b$ are divided into two subgroups (Parts 1 and 2) with different product specifications.

[b] Group BIII covers glazed tiles only. There is a low quantity of dry-pressed unglazed tiles produced with water absorption greater than 10 % mass fraction, which is not covered by this product group.

In **Table 1-2**, conversely, commercial names of ceramic tile products are reported with the main destination of use and the corresponding ISO 13006 classification (Busani, Palmonari and Timellini, 1995).

Table 1-2. Commercial names of ceramic tiles. Definitions: W: wall covering; F: floor covering; Int: internal; Ext: external.

Product	**WA %**	**Shaping method**	**Destination of use**	**ISO 13006 classification**
Majolica	15-25	Pressing	W/Int	BIII
Cottoforte	7-15	Pressing	F/Int	BII$_b$ - BIII
Monocottura light	0-6	Pressing	F/Int - F/Ext	BI - BII$_a$
Monocottura red	0-15	Pressing	F/Int - F/Ext	BI - BII - BIII
Monoporosa	10-20	Pressing	W/Int	BIII
Klinker	0-6	Extrusion	F/Int - F/Ext W/Ext	AI - AII$_a$
Cotto	3-15	Extrusion	F/Int - F/Ext	AII - AIII
Red stoneware	0-4	Pressing	F/Int - F/Ext	BI - BII$_a$
Porcelain stoneware	0-0.5	Pressing	F/Int - F/Ext W/Ext	BI$_a$

1.1. The Italian ceramic tile sector

Italy is among the major producers of ceramic tiles in the world with a seventh place as manufacturing country and with a fourth place in the export market in 2022. The first global producer is China, with a total output of 10.146 mln m^2, equal at the 48% of world's production, followed by India, with 1.897 mln m^2 and Brazil, with 867 mln m^2, according to 2022 data. In the same year, Italy produced 435 mln m^2 of ceramic tiles, while exporting 364 mln m^2, almost the 84% of the total national production (Acimac and Mecs, 2022).

Almost the entirety of the Italian production of ceramic tiles is located in the *Sassuolo* ceramic district, stretching over the provinces of Modena and Reggio-Emilia, in the Emilia-Romagna region in the north of Italy, as illustrated in **Figure 1-1**. The ceramic district is constituted by a vast aggregation of industrial entities mainly dealing with ceramic tiles and ceramic materials, responsible for the 81% of national production of ceramic tiles in 2019.

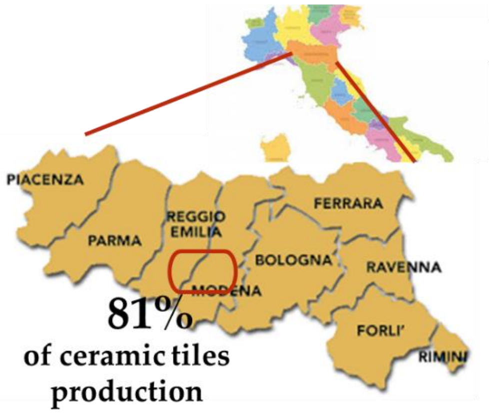


Figure 1-1. Location of the *Sassuolo* ceramic district in the Emilia-Romagna region.

Last available data from the industry show as, in 2019, the 87% of the sales for the Italian ceramic market has been led by porcelain stoneware tiles, while its contribution to the production was even nearly the 89% (*Indagine statistica sull'industria italiana - piastrelle di ceramica - Confindustria Ceramica*, 2019). Therefore, it is easy to understand how this product stands as a pillar for the Italian economy and how investments from companies are year by year so important.

Porcelain stoneware arrived on Italian market in the late 70s and, since then, thanks to its great technological performances and its high esthetic features, beat competitors and drove many companies to adopt this production.

Porcelain stoneware tiles are characterized by high mechanical strength and low water absorption, which makes these tiles the perfect solution for both internal and external covering for housing, as well as for high traffic areas or environments characterized by extreme humidity levels, as pools and bathrooms. Additionally, over the years, the shapes and sizes of tiles have been transforming, increasing the dimensions from more classic 30x30 or 60x60 cm formats, to ceramic slabs of 120x240 or 120x320 cm. Together with the introduction of high precision cutting and squaring operations and surface treatments machineries, the current larger sizes of tiles aim at the reduction of material use during the laying phase and of space between pieces, while improving the aesthetic of installations.

Another important process innovation which has enabled formidable aesthetic effects and thanks to which porcelain stoneware is actually leading the market, is the introduction of the digital decoration. Nowadays, almost the entirety of ceramic factories in Italy have adopted this software-controlled technique, and the range of achievable surface effects (marble, travertine, wood, concrete, metals, etc.) has become incredibly vast and the spectrum of decoration patterns basically infinite.

Nonetheless, even if certain ceramic products have disappeared from the Italian market, or have shifted to artistic or craftmanship productions, as *majolica*, there are varieties of ceramic tiles that are still industrially produced to some extent. In 2019, in fact, *monocottura* retained 5% of the Italian production, particularly at 3% for floor coverings and 2% for wall coverings, while the share of ceramic products characterized by a double-firing layout, as *majolica*, *cottoforte* and other earthenware tiles, amounted to another 5% (*Indagine statistica sull'industria italiana - piastrelle di ceramica - Confindustria Ceramica*, 2019).

As illustrated in **Figure 1-2**, the shares of *monocottura* tiles and of other products on total national production seem to have been continually reducing from 1999 to 2011. On the other hand, over the last decade, their representation has been remaining quite constant.

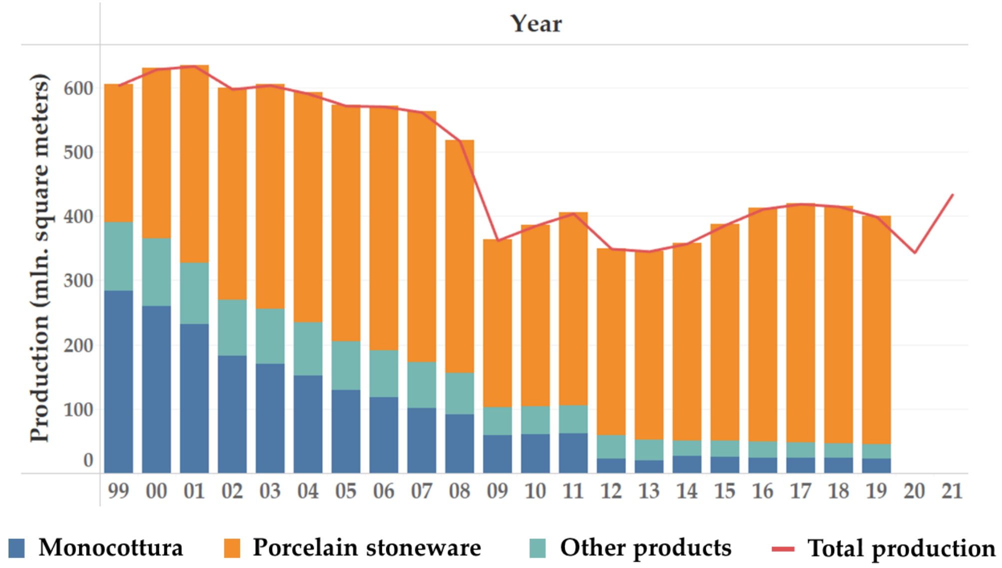


Figure 1-2. Total Italian production of ceramic tiles divided accorded to main products, for the period 1999-2021. Data on product were not available for years 2020-2021 (data from Acimac & Mecs, 2022; *Home - Confindustria Ceramica*).

However, the total Italian production of ceramic tiles has been decreasing since 2001, especially after the financial crisis of 2008, which has strongly impacted on the building sector. After that, the ceramic sector seemed to have timidly recovered, when another hit on national production was stroke by COVID-19 pandemic, even if, only the year after, tiles output returned to the values registered in the pre-pandemic period.

1.2. Raw materials for ceramic tiles

In a traditional ceramic body are present the first seven elements of the periodic table that are most contained inside the Earth's crust. The main constituents are Si and Al, with lower percentage of Na, K, Fe, Mg and Ca. Glazes are characterized by other elements as Pb, Zn, Sn, Cr, V, B, Zr, Ni (**Figure 1-3**). All of them are present as the corresponding oxides both in bodies, engobes, frits and glazes. These elements can combine in different manners giving a large number of crystalline structures and amorphous materials or, also, more or less complex mixtures of them. It is the case of naturally occurring minerals and rocks as well as synthetic materials created for specific purposes and used in the ceramic manufactory.

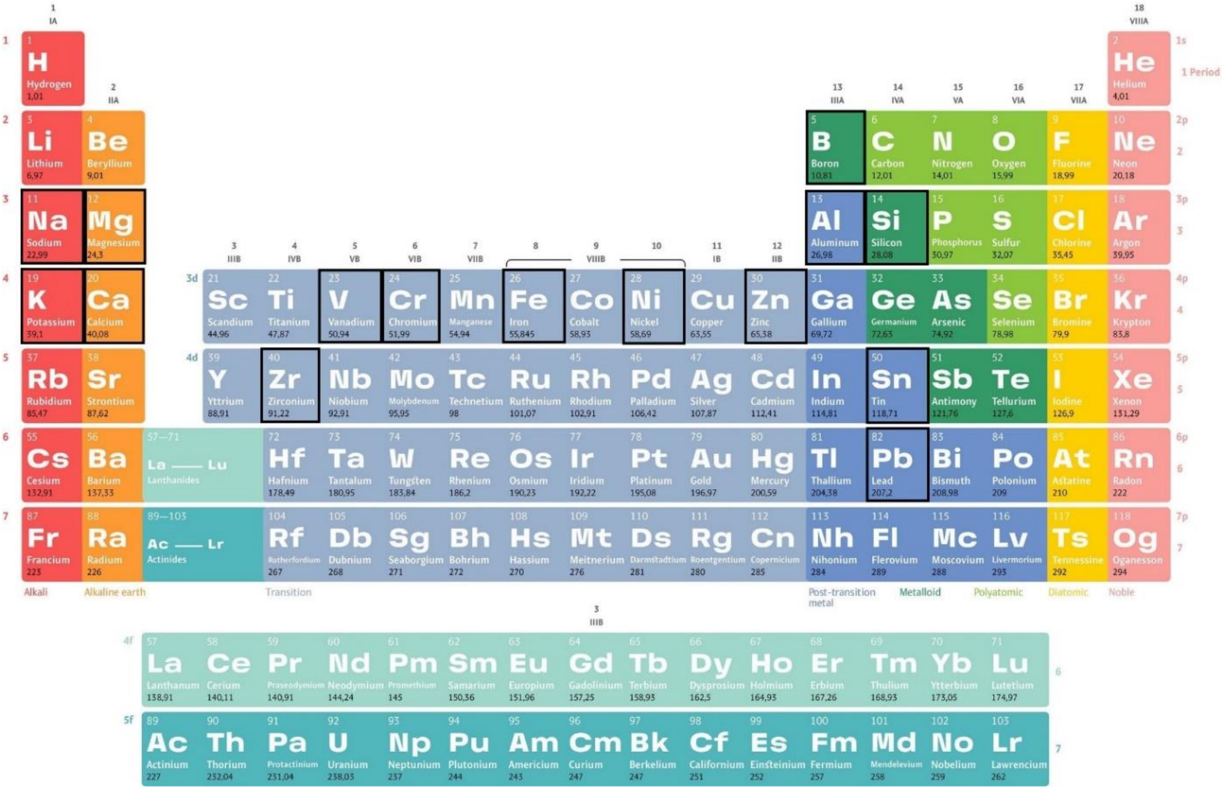


Figure 1-3. The periodic table of the elements. The most occurring elements in ceramic bodies and glazes have been enlightened.

Thus, the amount and nature of raw materials used in the tile industry are incredibly varied. Almost the whole totality is represented by rocks while a minor part by synthetic materials, as frits, involved in the production of glazes and engobes and by synthetic or natural organic compounds used as additives in batches and, hence, in small percentages.

Each ceramic product is characterized by a specific compositional range of raw materials which changed and broadened during times thanks to the birth of new products and the improvements of features of old ones. Another reason for this change is related to the worldwide spread of the ceramic industry and the following technological burst. In fact, when the manufacture of ceramic was predominantly a craftsman job and the production restricted to cities or small regions, the availability of materials was poor and limited only to nearby territories. Today, the increasing trade import allowed producers to use rocks and sands of a totally different composition from that coming from local extraction points.

This was the event, together with a deeper scientific knowledge of the process parameters of ceramic tile manufacture, that led to the overtaking of products such *majolica*, existing since centuries, by new ones as *cotto*, *cottoforte*, white and red *monoporosa*, *clinker* and, more recently, by *porcelain stoneware*.

Porcelain stoneware is also known as triaxial porcelain because it displays a vitrified body with almost zero open porosity, like porcelain, and its composition is a mixture of three main components: clay, fluxes and fillers.

- **Clays** ensure plasticity and good mechanical properties of unfired tiles while during firing, depending on the specific composition in minerals, can act as flux and as mullite precursor.

- **Fluxes** form eutectic systems together with clays and quartz leading to a liquid phase at high temperature that allow the densification of the ceramic body by viscous flow.

- **Fillers**, above all quartz, provide the so-called *skeleton*, that is a coarse-grained structure contrasting deformation and shrinkage during drying and firing stages.

These materials are more or less complex mixture of inorganic oxides with limited impurities of organic matters and other inorganic compounds like sulfides, sulphates, chlorides and carbonates. For a more chemical point of view, it can be affirmed that the most present eight oxides are responsible of:

Al_2O_3	refractoriness and plasticity
SiO_2	structure and skeleton of the ceramic body
Fe_2O_3 and TiO_2	color and, sometimes, fluxing properties
CaO and MgO	shrinkage control through the formation of silicates of Ca and Mg and fluxing properties
K_2O and Na_2O	fluxing properties

The differences between the production of porcelain stoneware tiles and more traditional ceramic ones lie in the process parameters, among which the firing cycle is the most important, and in a specific range of composition of the raw materials involved (Zanelli *et al.*, 2011), as illustrated in the ternary diagram in **Figure 1-4**.

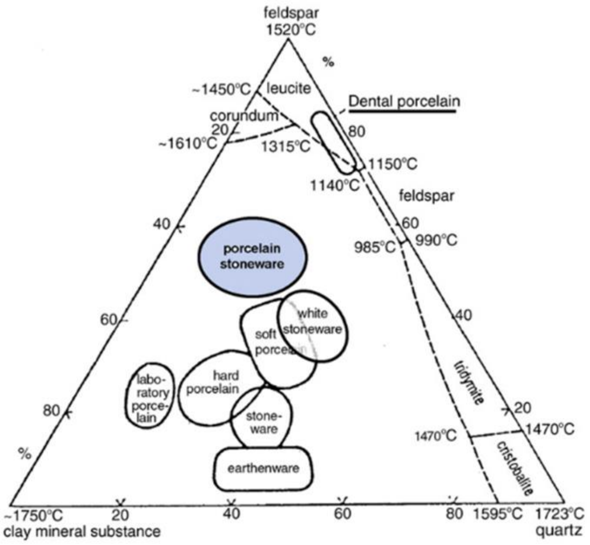


Figure 1-4. Range of composition of porcelain stoneware in the clay-feldspar-quartz ternary diagram (from Zanelli *et al.*, 2011).

In the specific case of porcelain stoneware tiles, the use of larger amounts of fluxes and clays displaying a well-balanced ratio of expandable and refractory components is the key to the obtainment of a ceramic body characterized by a very compact microstructure and an open porosity closed to zero (Galos, 2011). These two features ensure all the outstanding technological properties by which porcelain stoneware tiles are so famous and widely commercialized.

In the following chapters, the most used raw materials in the production of ceramic tiles will be described, with a particular focus on their adoption in porcelain stoneware and on how their composition affects the technological features of final products.

1.2.1. Clays

Clay is a soft, loose, earthy material combining various clay minerals with a grain size often lower than 2-4 μm, all belonging to the silicate class of phyllosilicates. Actually, the genesis of these materials is quite differentiated and can be of a sedimentary nature or due to a low-grade metamorphism on existing rocks. As a general scheme, it can be considered a specific area that can be altered mechanically and chemically by the combined action of rain, wind and freeze-thaw cycles. The products of these alterations are transported by the same atmospheric agents in water, giving birth to sedimentation basins. Thus, these latter are modified following orogenetic movements or by lithification and diagenesis (Dondi and Bertolotti, 2021). Later on, processes of cationic substitution can act together with the repeated action of pressure and temperature, leading to the formation of new minerals (metamorphism). It can be so stated that the variety of clays is enormous, according to the different combination of the initial rocks, climatic and morphological conditions and time and nature of applied physical forces.

The crystal structure of clays can be described as the recurrence of a silicate sheet of SiO_4^{4-} tetrahedra (T) and an aluminate sheet of $Al(OH)_6^{3-}$ octahedra (O), reciprocally alternating according to specific patterns. In this arrangement, the hydroxyl group (OH^-) of each octahedron is replaced with the oxygen atom at the top of each tetrahedron, in this manner being shared by the two layers in **Figure 1-5**. As a consequence, the whole structure results neutral. These units of repetition are separated by a well-defined inter-space that can often hosts water or alkaline ions as Na^+ and K^+ depending on its dimensions, which usually ranges from two to eight or more Angstroms (1 Å=1 * 10^{-10} m).

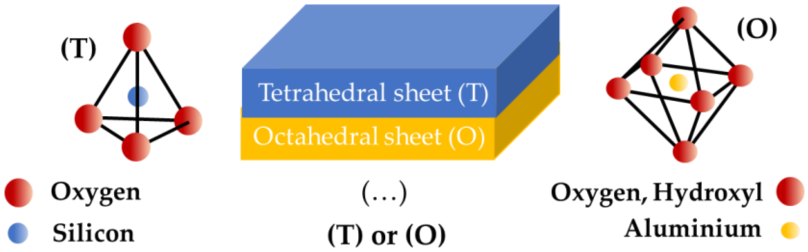


Figure 1-5. Schematic representation of the crystal structure of minerals belonging to the clay family.

Hydrogen bonds and Van der Waals forces are among the interactions accounting for the reciprocal cohesion of the layers, while the occurrence of interstratified ions adds an electrostatic component to these forces. The presence of water between clay particles allows them to slide over each other, granting the so-called “plasticity”. In addition, together with the abundance and nature of other ions, the possibility of hosting water defines the different varieties of clays. All these variables are governed by the geological history of a specific clay mineral.

In the following sections, the most representative minerals of the class of clays will be described, before addressing the discussion on the main clayey raw materials employed in the production of porcelain stoneware.

1.2.1.1. Kaolinite

The crystalline structure of kaolinite is organized by the alternation of a simple repetition unit composed by the coupling of a silicate tetrahedral layer and an aluminate octahedral layer (**Figure 1-6**).

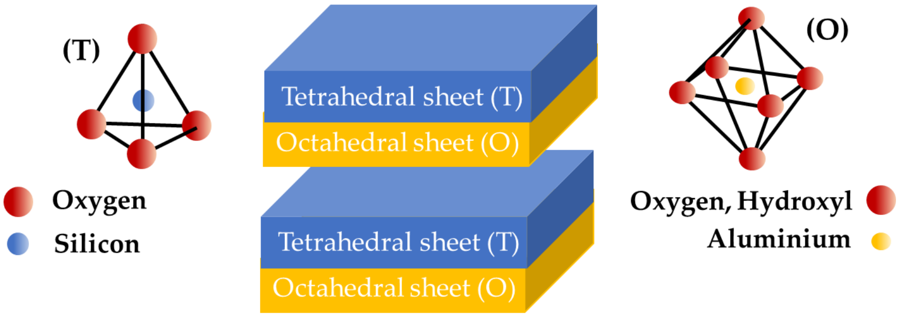


Figure 1-6. Schematic representation of the crystal structure of kaolinite.

The chemical composition is represented by the formula $Al_2Si_2O_5(OH)_4$.
The theoretical composition is SiO_2= 46,5%, Al_2O_3= 39,5% and H_2O= 14%.
No water or other ions are present between the sheets. This lack accounts for the low plasticity and the high refractoriness displayed by clays containing high amounts of this minerals. However, the silicon ions Si^{4+} can be sometimes substituted by other ions, as Al^{3+} or Fe^{3+}, leading to a charge deficiency in the structure. The extent of this substitutions, as happens for any other materials displaying a defined crystalline structure, has a strong impact on the mechanical and electric properties of kaolinite (Kallay, 2000).

It is a soft, earthly and usually white minerals, characterized by a quite unctuous surface. Its origin takes place from the transformation of feldspars present in rocks, after the displacement of alkaline elements. However, this mineral is found in deposits as a mixture of kaolinite, quartz, untouched by the physical and chemical ageing, feldspars, as a result of incomplete alteration phenomena and, in some cases, iron oxides, responsible for the rusty color sometimes displayed by the material, and micas. The deposits are generally of primary origin which means that no transportation has taken place and they are found near the primitive rocks. In the case of deposits of secondary origin, the material has been transported and allotted in aquatic environments allowing both the selection of finest particles and the inclusion of other organic or inorganic elements. Kaolinite is one of the most common minerals to be present on the Earth and it is mined almost everywhere. However, amongst the biggest producers there are USA, Uzbekistan, Czech Republic, Germany, Republic of Korea and then Brazil, Ukraine and United Kingdom, while Italy is the twelfth world producer (*Mineral Resources Program | U.S. Geological Survey*). It is employed in the industry of rubber as a charging material and in that of paper with the same purpose and as surface coating. Yet the most important application for the present scope, can be found in "ball clays" and "china clays", two raw materials rich in kaolinite and widely used in the ceramic manufacture.

In the production of porcelain stoneware tiles, the role of this mineral is particularly crucial. In fact, kaolinite allows the formation of mullite ($3Al_2O_3{\cdot}SiO_2$) inside the ceramic body and for this reason it must always be present in clay raw materials. It naturally occurs with different grades of structure order providing, in turn, different behavior of the mixture during the sintering process. The dehydroxylation processes occurring in kaolinite, normally in the range from 530 and 630 °C, lead to metakaolin, a complex amorphous structure characterized by a certain long-range order due to layers stacking. As the results of other phase transformations, mullite is formed in crystals whose shape and number largely depends on the nature and amount of kaolinite in the raw material (Bellotto *et al.*, 1995; Lee, Kim and Moon, 1999). However, the absence of interstratified water and alkaline or alkaline earth ions that could have led to a possible fluxing action, induces a definitely low plasticity and an important refractoriness in this mineral. A ceramic product employing high percentage of kaolinite, as porcelain for example, is characterized by firing temperatures of 1300-1400 °C, much higher than those displayed by porcelain stoneware, typically ranging from 1150 to 1250 °C. For these reasons, the proportion between kaolinite and other more plastic components, as illite or smectite, in porcelain stoneware batches must be carefully balanced in order to promote optimum sintering outcomes. In fact, the mineralogical composition is one of the main ruling factors controlling the crystalline phases inside the ceramic body as well as the volume of the vitreous phase and, to the greatest extent, for the closed porosity and bulk density values. Lowering the first term while increasing the second with a concomitant great mullite evolution is thus made possible through the use of raw materials containing the proper amount of kaolinite.

1.2.1.2. Illite

The term *Illite* accounts for a group of closely related non-expanding minerals nowadays not yet completely identified. Some scientific works consider these minerals to be similar to micas while others relate them as a particular type of muscovite. Some illites are described by the alternation of repetition units composed by two tetrahedral layers accommodating an octahedral one between them (trioctahedral illites), as illustrated in **Figure 1-7**. Others are characterized by the repetition of only one tetrahedral and one octahedral layer (dioctahedral illites) (Rieder *et al.*, 1998). Thus, the ratio SiO_2/Al_2O_3 is found ranging from two to four. The silicon cations are always substituted to a certain extent by aluminum, with potassium balancing the overall charge of the reticule. The structure of these minerals, in addition, can sometimes accommodate interstratified water.

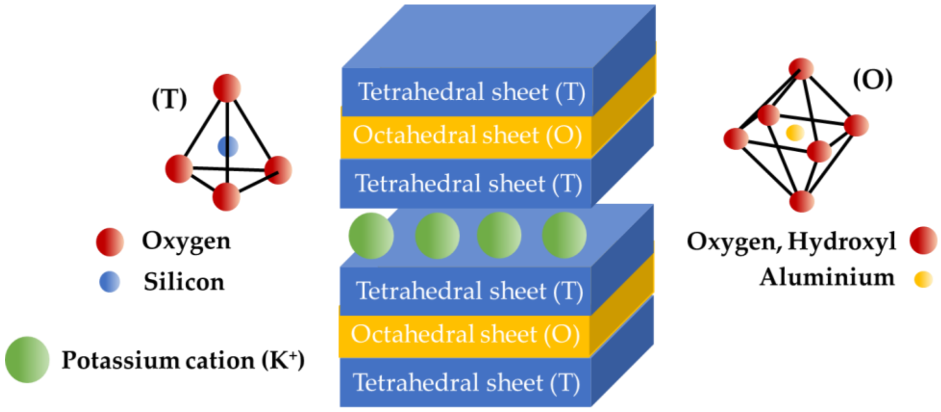


Figure 1-7. Schematic representation of the crystal structure of illite (trioctahedral illites).

The chemical composition can be represented by the formula $K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$.

It is a greasy and earthy material of gray-white to greenish-gray colors. Weathering and chemical alteration in hydrothermal alkaline environments followed by sedimentation account for the origin of illite. It is generally found associated with quartz, calcite and dolomite as well as with others sedimentary and low-grade metamorphic rocks as chlorite, smectite and kaolinite. Thus, illite is represented from low to great extent in almost every clay employed in the ceramic manufacture. However, among the raw materials most rich in these minerals, the Ukrainian ball-clays stand out as a particularly suited ingredient for the production of porcelain stoneware tiles.

One of the main reasons for the large use of illitic clays is their high plasticity, essential for the early stages of the tile-making process. In particular, this feature becomes fundamental in improving the rheological behavior of ceramic slips, allowing in this manner a better mechanical agitation of mixtures and a valuable spray-drying process. Higher flexural strength values for green and dried bodies can be pointed out as another important consequence of the presence of these minerals. However, the illite content in clays is also crucial during the firing process stage because it contributes, together with the fluxing portion, to the formation of the glassy phase due to its high potassium content. This large amount of melt has been proved to have a sensible role in the inhibition of mullite formation (Ferrari and Gualtieri, 2006). Thus, illite becomes essential especially in raw materials displaying important amount of kaolinite or other refractory minerals because of the possibility in balancing the opposite effects of these latter components (Galos, 2011). Illite can sometimes be found in association with smectite in interstratified layers, boosting in this way its water absorption capability, otherwise quite low. Clays containing this type of mineral, known as interstratified illite/smectite, are likewise widely adopted for the same purposes but with rather enhanced effects.

1.2.1.3. Smectite

The term *Smectite* accounts for a large group of minerals displaying a large specific surface area and exhibiting a high expansion capability in presence of water. These clays are characterized by a trioctahedral structure in which the octahedral layer lays between two tetrahedral planes (**Figure 1-8**). As a consequence, there are no hydroxyl groups able to participate in hydrogen bonding and the sole forces to be present are the mild Van der Waals interactions. Thus, water can be easily accommodated between the clay particles. Another important feature of these minerals is the high cation exchange capacity, that is the ability in substituting ions inside the reticule. In fact, silicon can be replaced by aluminum ions inside the tetrahedra while other species as bivalent magnesium or trivalent iron can replace these latter inside the octahedra. The overall neutrality is then reached through the embodiment of alkaline or alkaline-earth ions between the layers. The most common members of the group of smectite are montmorillonite, nontronite and saponite.

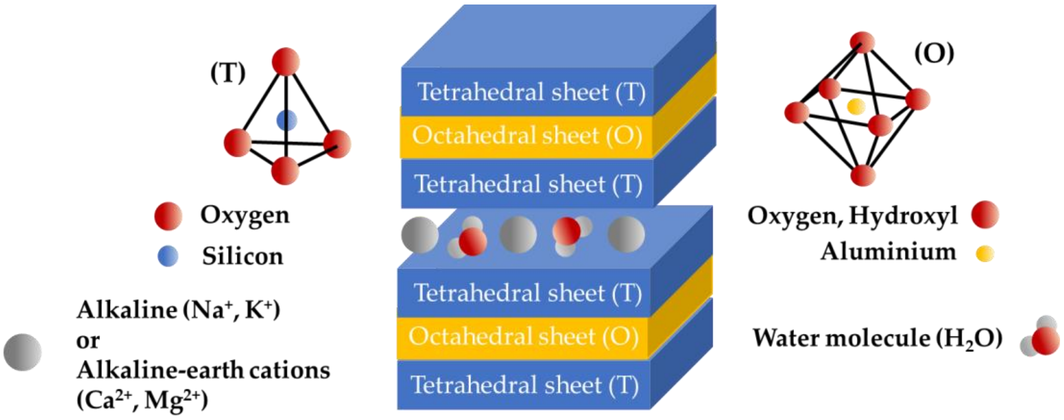


Figure 1-8. Schematic representation of the crystal structure of smectite.

The chemical composition cannot be defined exactly because of the high number of the different existing minerals. However, the chemical formula of the three above mentioned species is reported as example (*Mindat.Org*).
Montmorillonite: $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2$ x nH_2O
Nontronite: $(CaO_{0.5}Na)_{0.3}Fe^{3+}_2(Si,Al)_4O_{10}(OH)_2$ x nH_2O
Saponite: $Ca_{0.25}(Mg,Fe)_3((Si,Al)_4O_{10})(OH)_2$ x nH_2O

The origin of these minerals is mainly related to the chemical and physical alteration of primitive igneous rocks while deposits of a sedimentary nature are also relevant. Some researchers have observed that clay materials rich in interstratified illite and smectite, together with bentonites, becomes progressively rich in the first mineral and poorer in the second one by increasing the depth of burial in sedimentary basins. This process, known in the literature as smectite illitization, has been proved to be influenced mainly by time, availability of potassium and fluid circulation (Bethke, Vergo and Altaner, 1986; Cavalcante *et al.*, 2007). Raw materials containing smectite minerals in moderate percentage or interstratified illite/smectite clays are widely employed in the ceramic industry as well as in the manufacture of porcelain stoneware tiles.

Together with illite, the presence of smectite contributes in forming the glassy phase in the ceramic body, assuring in this way a good densification process. In fact, the low structural order and the great specific surface area of smectite particles lead to a high reactivity of formulations. For this reason, these two minerals play a critical role whenever an important fraction of a more refractory component, as kaolinite, is detected in a clay by the mineralogical analysis. Nevertheless, materials containing exclusively smectite minerals are hardly used for this purpose because their high swelling capacity which is notably negative on the rheological behavior of ceramic mixtures.

1.2.1.4. Chlorite

The term *Chlorite* describes a group of micaceous phyllosilicates minerals. The structure of these clay minerals is defined through the alternation of a mica-like layer, where an octahedral plane of aluminum or magnesium lays between two silicate tetrahedral layers, and a brucite-like one (**Figure 1-9**). This latter is formed by two sheets of closely packed hydroxyl groups providing the octahedral coordination sites for the different ionic species, as bivalent magnesium or trivalent iron or aluminum, defining the different minerals of this group.

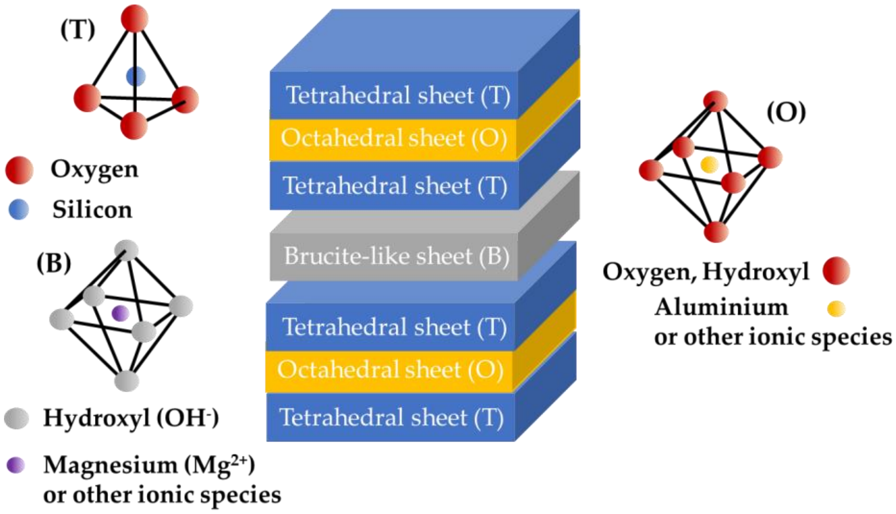


Figure 1-9. Schematic representation of the crystal structure of chlorite.

The chemical composition can be generally described by the formula $M_{4-6}T_4O_{10}(OH,O)_8$, where M= Al, Fe^{3+} and Fe^{2+}, Li, Mg, Mn, Cr, Ni and Zn and T= Si, Al, Fe^{3+}, Be and B (Haldar, 2020).

In turn, this group of clay minerals can be divided in orthochlorites, rich in magnesium, and in leptochlorite, rich in iron. The alteration of primitive igneous rocks rich in ferromagnesian minerals and the occurrence of some metasomatism phenomena involving the addition of these elements into the rock mass, can account for the origin of chlorites. These clays are never found pure but together with quartz, feldspars, in shist assemblages or in association with talc.

This kind of raw material is widely used in the ceramic manufacture and primarily in the Italian industry because of the high relevance of these minerals in clays coming from the Apennine area in the Emilia Romagna region. In fact, an enhancement of the densification kinetics of porcelain stoneware tile bodies during firing is often pursued through the addition of some magnesium-bearing materials as chlorite or talc and dolomite. In some cases, the sintering processes of this type of tile have been seen to proceed much faster with the use of chlorites rather than with talc because in the former case the magnesium results more accessible than in the latter (Biasini *et al.*, 2003).

Furthermore, in chlorites a proper magnesium oxide content inside the mixture is reached only by using an appropriate clay, avoiding in this manner the use of other raw materials which could sometimes lead to adverse effects.

1.2.1.5. Talc

Talc is a magnesium phyllosilicate displaying a mica-like structure of two silicate tetrahedral layers accommodating an octahedral plane of magnesium (**Figure 1-10**). Variable amounts of iron, aluminum, manganese, nickel or fluorine can be contained as impurity, strongly affecting the properties of this material (Fiume *et al.*, 2015).

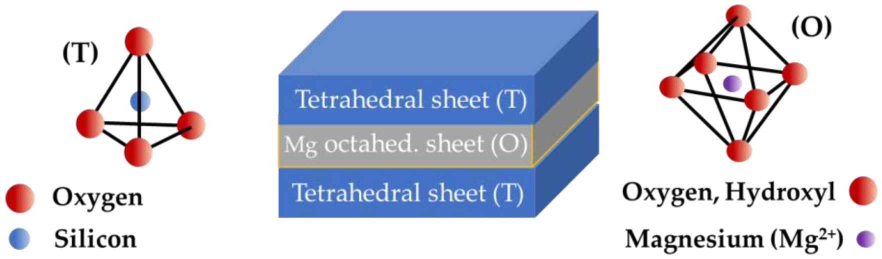


Figure 1-10. Schematic representation of the crystal structure of talc.

The chemical composition is represented by the formula $Mg_3Si_4O_{10}(OH)_2$.

Talc can be present in almost every color, depending on the extent of impurities. It has a predominantly plate-like structure, with adjacent layers very weakly bonded by Van der Waals forces. As a consequence, it is easily sheared along the plane explaining its natural slippery feel as well as its softness. In fact, talc is the softest amongst mineral, and it is set as standard 1 of the Mohs Hardness scale.

Two main origins of this mineral can be identified. One is the metamorphism of magnesian minerals such serpentine, amphibole and olivine, together with it is sometimes founded. The second is as a result of the reaction between acidic solutions rich in silica and dolomite or magnesite in hydrothermal environments.

Although talc is produced worldwide, the major deposits are situated in the Asian continent making China and India the two main producers. Other big exporters are Brazil, USA and South Korea (*Mineral Resources Program | U.S. Geological Survey*).

Nowadays, talc has been replaced in the paint and cosmetics industry in response to health concerns and litigations. In fact, this mineral has for long time raised suspicions regarding its role on certain types of diseases, mainly cancers of the ovaries and lungs. It is classified as a group 3 agent in the IARC listing (*List of Classifications – IARC*). This is mainly related to its association with asbestos because it has been often founded in underground ore together with deposits of this latter fibrous silicate minerals. There still are controversies regarding its safety as some studies have claimed a link between talc and cancer while others have not (Henderson *et al.*, 1971; Harlow and Hartge, 1995). Notwithstanding this debate, talc is still used in the ceramic manufacture as a component of some mixtures for porcelain stoneware tiles, even if in small quantities.

The reason for that can be founded in its high magnesium oxide content. In fact, talc is able to form eutectic mixtures with sodic and potassic feldspar, expressing in this way an important fluxing behavior (Magagnin *et al.*, 2014). However, its percentage are always kept as low as possible because of the related great effect in decreasing the viscosity of the liquid phase in sintering. A too much low level of viscosity can drive to some problems such as a high pyroplasticity and an increase in the total porosity of the body. On the other hand, the use of talc is normally related to a relevant decrease in the open porosity providing porcelain stoneware tiles displaying such feature an optimum surface stains resistance (Dondi *et al.*, 2005). Another consequence of the introduction of this mineral in ceramic mixtures, is represented by its negative effects on the rate of formation and total content of mullite. For this same reason, the use of talc is promoted when clays displaying high amount of kaolinite are employed in the production of stoneware tiles because it can balance the negative effects on the sintering kinetics and mechanical resistance of dried bodies expressed by this latter mineral.

1.2.1.6. Clay raw materials

The clay raw materials commercialized for the production of porcelain stoneware tiles are, thus, a series of natural occurring aggregates containing the above-mentioned minerals together with some other oxides and components. Even if in small percentages, such minor components can lead to undesired reactions inside the ceramic bodies, having a strong effect on the mechanical or aesthetic properties of finished products. Among these, there are Fe_2O_3, TiO_2, $MgCO_3$ and $CaCO_3$ together with some sulfides and soluble salts. In addition, the presence of organic matter, found as impurity especially in clays, rather than in fluxes or quartz components, must be taken under strict control.

The most used clay raw materials for the production of porcelain stoneware tiles are the so-called ball-clays defined as "*a fine-grained, highly plastic, mainly kaolinitic sedimentary clay, the higher grades of which fire to a white or near white color*" (Wilson, 1998). During years, such a definition has been stretched to cover a vast range of mineralogical compositions and technological properties making a rigorous description of these materials almost hopeless. However, there are some recurrent characteristics of ball-clays that must be here outlined. Kaolinite varies from 25 to 75% and it is always accompanied by significant amount of illite, sometimes up to 60%, while expandable components are often present as interstratified illite/smectite and, sometimes, as smectite. Generally, these materials are characterized by a fine-grained particle size distribution with the clay fraction over 50% and frequently over 75%. The technological properties are largely diversified because of the corresponding percentages of the different minerals and, also, by the contemporary presence of feldspars and quartz in various concentrations (Dondi, Raimondo and Zanelli, 2014).

However, the variety is not limited to ball-clays. As was previously noticed, the essential roles for a clay inside mixtures for porcelain stoneware, are those of reaching a proper plasticity and contributing to the mechanical properties of fired products. These features can then be easily satisfied by mixing low plasticity clays as, for examples, high or medium grade kaolins, with a more plastic components as bentonites. In this regard, the Methylene Blue Index (MBI) together with the detection of the Atterberg limits are the most powerful tools for predicting the technological performances of clays (Chiappone *et al.*, 2004; Schmitz, Schroeder and Charlier, 2004).

1.2.2. Fluxes

Feldspathic minerals, or feldspars, are the most important fluxing agent in the ceramic industry. Belonging to the family of tectosilicates, these minerals account for the 41% of the entire mass of the earth's crust (Anderson and Anderson, 2010). They are characterized by a ring structure composed of four tetrahedral groups, the nature of which largely depends on the mineral kind. Usually, in potassic or sodic feldspars, there are three silicon tetrahedra and one of aluminum, while in calcic ones, there are half of silicon and half of aluminum. A schematic representation of the crystal structure of a classic feldspar is represented in **Figure 1-11**. Owing to their interlocking structure organized by a broad interconnection of strong covalent bonds, tectosilicates minerals as feldspars display high hardness values (from 6 to 7 on the Moh's Hardness scale).

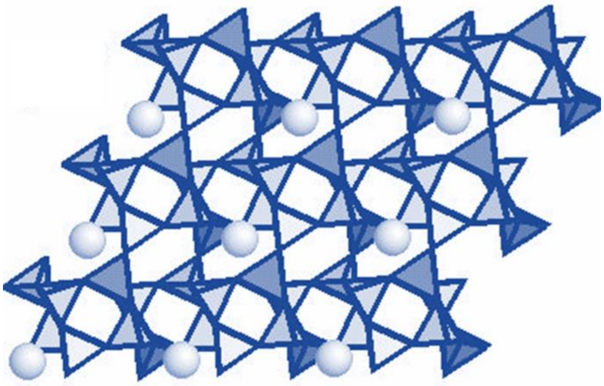


Figure 1-11. Schematic representation of the crystal structure of feldspars, from (*Geos 306, Fall 2004, Lecture 13, The Crust*, 2022).

The general chemical formula is: XY_4O_8 where X= Na^+, K^+, Ca^{2+}, Ba^{2+} and other less common ions, and Y= Si^{4+} or Al^{3+}.
The elemental composition of the extreme variety of feldspars, can be expressed in terms of three endmembers, being also among the most occurring minerals of the family: orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). For examples, the plagioclase series embraces a broad number of solid solutions whose endmembers are albite and anorthite.

Pegmatite, albitite, aplite and granitic rocks are among the most important sources of fluxes (Dondi, 2018). Due to their high amount of feldspathic minerals, displaying a strong fluxing action, these rocks are the main components of ceramic mixtures for vitrified bodies as porcelain stoneware. They all display an intrusive igneous origin and are also referred as acidic rocks because of the high percentages of SiO_2 inside their mass. Generally composed by feldspars, together with quartz and other components, the raw materials are mineral aggregates presenting crystals in variable sizes with often large dimensions and whose body color is strongly related to the different nature of these latter.
The corresponding basic rocks are also widely employed as fluxes. Among these, there are some effusive igneous rocks, as basalt and andesite, and other intrusive ones as diorite, gabbro and anorthosite. The content of SiO_2 in these rocks is quite low, whereas elements as Ca, Mg and Fe can be highly represented, accounting for their often-dark colors.
Among the other sources of fluxes, a paramount role is also performed by feldspathic arenites, some metamorphic rocks, as phyllites and porphyroids, and others coming from hydrothermal alterations, as eurite and sericitic rocks. In certain cases, aggregates containing minerals not belonging to the tectosilicate's family are employed as fluxing agents, as is the case for talc and talch-chlorite formations and diopsidite (Dondi *et al.*, 2019).

Nonetheless, even if the number and presence of rocks that can be used to perform a fluxing action is somewhat enormous, it must be said that the alkali feldspars, particularly Na and K feldspars, are the best-known fluxes for the ceramic industry and, for that reason, among the most appealing raw materials. The rapid gaining market for porcelain stoneware tiles, together with the constantly increasing technological improvements in its production, resulted in a corresponding increase in the extraction activity of feldspathic rocks, with a particular boost in the production of high-value feldspars. The primary source of fluxes for the Italian ceramic tile industry is represented by albitites, which exploitation has been increasing by ten-fold since

1994, following data reported by Dondi, 2018. Such extreme employment of this mineral is related to its optimum fusibility and very low presence of iron and titanium impurities, two perfect characteristics for its adoption as the main flux inside porcelain stoneware pastes. Turkey is the major global exporter of albitites, in virtue of the great deposits in the Menderes massif region, almost retaining a monopoly role as a supplier of fluxes amongst porcelain stoneware tile manufacturers in Europe. It is important to highlight here as the commercial dependence to singular countries should never be accorded, in order to avoid excessive dependency to monopolies and vulnerability to unforeseen social and political events. In addition, even if being feldspars the most occurring minerals on the planet, its most valuable representants cannot withstand alone the increasing trend in exploitation. Elseways, fluxes with medium to low fusibility, as is the case of granitoids, feldspathic sands, aplites and pegmatites, are believed to occur with large resources, but are unable to satisfactorily substitute low melting fluxes as sodium feldspars.

In this context, it is of paramount importance the continuous exploration of new exploitable ores and the accurate evaluation of existing reserves to grant a diversified and continuous secure future supply of fluxes suitable for ceramic production. Furthermore, it is suggested as another important action to reduce excessive consumption of high purity feldspathic minerals can be implemented by working to relax technological constrains in ceramic tile production. In particular, a crucial challenge for scientific research will be to develop ceramic bodies able to withstand a lower grade of purity and the presence of iron without excessively affect firing behavior (deformation and bloating) and aesthetical defects. At the same time, researchers shall direct major efforts to the mastering of alternative and more environmentally sustainable sources of fluxes as, for example, recycled glass, as it will be illustrated in the next sections.

The main role of a flux component is to form a liquid phase granting the partial vitrification of the ceramic body by viscous flow sintering (Zanelli *et al.*, 2011). Hereof, feldspathic materials are able to form eutectic liquid phases with other minerals that are present in ceramic batches. For this reason, these raw materials are employed in mixtures for porcelain stoneware tiles in high proportions, even up to 60% in weight. In order to understand the potential fluxing action of the different raw materials, some characteristics have to be addressed with particular concern. In particular, of primary importance is the thermal behavior of the flux source, which is normally described for the scope through hot stage microscope (HSM) analysis. Critical parameters are the softening temperature (T_{soft}) and the hemisphere temperature (T_{melt}), addressing the beginning of melting of one mineral phase inside the material and the beginning of the entire melting process, correspondingly (Dondi *et al.*, 2019). In fact, mixtures of minerals do not melt together but according to eutectic proportions and to kinetic factors upon firing.

The corresponding percentage of Na_2O, K_2O and CaO inside the flux source, is the main factor dictating the thermal behavior of fluxes. In fact, it has been demonstrated as the lowering of T_{soft} and T_{melt} parameters goes along with the increasing amount of the mentioned oxides which, ultimately, prompt the emerging of viscous flow events, granting optimum vitrification of the ceramic body. The iron content is still another important factor because high iron impurities are able to affect the color of porcelain stoneware pastes, contributing for dark tones, and to trigger bloating effects during firing.

1.2.3. Fillers

The main mineral adopted as fillers in the production ceramic tiles is silica, generally under the form of sands, which are the most abundant source of silica in nature.

The chemical formula of silica is SiO_2, and the base structure is formed by a tetrahedron of oxygen with a silicon atom at the center, as represented in **Figure 1-12**, together with the crystalline structure.

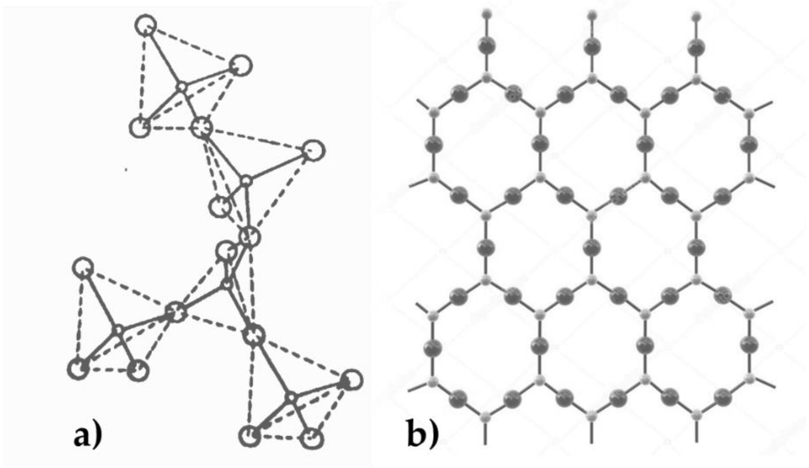


Figure 1-12. Structural arrangement of silica tetrahedra (**a**) and crystalline structure of silica (**b**).

Silica is naturally occurring under the form of crystalline quartz or in its amorphous arrangement in volcanic rocks as perlite and obsidian. Quartz, tridymite and cristobalite are the main crystalline structures of silica, which mutual conversion is strictly dependent on temperature and pressure. The key transformations are reported in **Table 1-3**.

Table 1-3. Main transformation of silica crystalline structure with temperature.

Quartz	→	Tridymite	870 °C
Quartz α	→	Quartz β	573°
Tridymite	→	Cristobalite	1470°
Tridymite α	→	Tridymite β	117/163°
Cristobalite α	→	Cristobalite β	220/270°

The most important is the transformation quartz α → quartz β at 573 °C, involving a structural rearrangement which corresponds to a total increase in volume. Normally, there are no problem related with the event during the heating stage of manufactures. Conversely, the same transformation can lead to some drawbacks during the cooling of pieces. In fact, the quartz grains, once embedded in the glassy matrix, can undergo cracks if the cooling phase is too fast, as a consequence of traction forces between the grains and the matrix (Carty and Senapati, 2005). Such event can at last result in the complete breakage of the ceramic manufacture.

Tridymite and cristobalite are hardly found in nature, with the exception of little inclusions in some igneous rocks, because their genesis is related to high temperatures and pressures far from ambient conditions. However, such crystalline entities can evolve during the firing process of ceramic manufactures.

In the past, physical treatment on fired tiles as, for examples, the cutting and squaring operations together with the handling of siliceous raw materials can potentially release fine particles of crystalline silica inside working environments contributing to the risk of silicosis, a lung disease caused by the inhalation of crystalline silica dust (Leung, Yu and Chen, 2012). Nowadays, post-firing operations on fired tiles are normally confined in closed working machineries involving water both as cooling fluid and dust trap, with the consequent low risk of dust evolution. Furthermore, workers are informed towards the risk of similar occupational diseases and furnished with the proper personal protective equipment. However, the monitoring of crystalline silica in working environments is mandatory according the European Directive (EU) 2017/2398, 2017 and exposure concentration limits are fixed at 0.1 mg/m^3.

The addition of a source of silica inside formulation for porcelain stoneware tiles has two main different purposes. In first place, by adjusting the alumina/silica ratio is possible to maximize the evolution of mullite during firing, a characteristic needle-shape mineral phase ($3Al_2O_3 \cdot 2SiO_2$) awarding high mechanical strength and an increased thermal shock resistance to ceramic products (Leonelli *et al.*, 2001). Secondly, the presence of quartz grains dispersed inside the glassy matrix helps reducing the dimensional contraction and retaining deformation during firing.

Such characteristics have been demonstrated to be strongly related to dimensions of particles. More in particular, a finer quartz particle size seems associated with an increased modulus of elasticity and a reduced size of flaws in grains after cooling. However, an excessive dissolution of quartz inside the glassy phase, resulting in a too small size of particles prevents the benefits on mechanical strength normally bestow by this component (Carty and Pinto, 2008; De Noni *et al.*, 2009).

Another important use of quartz is in the preparation of frits, where it is used in percentages ranging from 20 to 40%.

1.2.4. Other components

Together with clays, feldspars and sands, there are other minerals and components that can be found in batches for porcelain stoneware tiles. Such materials are not intentionally added to ceramic formulations but, on the contrary, are often directly associated with the above-mentioned minerals in natural ores as minor constituents or impurities. Among these can be cited iron oxide, titanium oxide, carbonates, mineral hydroxides, soluble salts, sulfides and organic matter. All these components have a negative impact during the production process of tiles, especially by affecting rheology of ceramic slips and by promoting undesired effects during firing. For this reason, it is of paramount importance to understand their role in order to avoid any predictable drawback caused by an improper selection of raw materials or by an erroneous setting of process parameters.

1.2.4.1. Iron oxide

Iron is easily found in raw materials for ceramic production. It is widely contained in clays under the form of goethite ($FeO(OH)$) or hematite (Fe_2O_3) and it is the major responsible for the color of fired bodies. For this reason, the clay raw materials are often classified as light-firing clays or dark-firing clays where the upper limit for the first ones is set to 3% of Fe_2O_3 content. The limit for the production of porcelain stoneware tiles is even more rigorous, generally fixed under 1% of Fe_2O_3 (Dondi, Raimondo and Zanelli, 2014). Further, the mechanical influence of this mineral on fired ceramic bodies is well known. For example, it has been proved that the presence of hematite has a detrimental effect on the mechanical resistance of tiles while iron can be hosted inside the mullite structure affecting some of its mechanical features (Ferrari and Gualtieri, 2006; Andji *et al.*, 2009). Another cause in this regard is found in its reduction by the combined activity of organic matter, sulfides and a too low oxygen content inside the kiln atmosphere, leading to the black-core effect, as it will be afterwards illustrated in detail. As a consequence, the amount of iron oxide in clays has to be strictly monitored in order to obtain products characterized by a high aesthetic value and by strong technological properties.

1.2.4.2. Carbonates

Carbonates are usually found in rocks under the form of calcite, $CaCO_3$, magnesite, $MgCO_3$, or dolomite $CaMg(CO_3)_2$. The origin of these minerals is quite differentiated, but it is often of a sedimentary nature. Such genesis relates to precipitation mechanisms of fine particles arising from oversaturated solutions or after the death of marine microorganisms characterized by carbonate shells. On the other hand, the physical and chemical action together with recrystallization events account for a metamorphic origin. Even if occurring in vast deposits most as pure material, carbonates are often associated with clays or quartz. They can prevail in some dark-firing clays even up to high percentages, reaching sometimes 50% on weight, while are normally present in limited extent in light-firing clays as kaolin or ball-clays (Dondi, Raimondo and Zanelli, 2014). The occurrence of carbonates inside ceramic bodies plays a complex role during the firing process, especially controlling the firing shrinkage and the thermal and moisture expansion. However, the amount of these minerals is kept as low as possible in mixtures for highly vitrified products, mainly because of their strong action in increasing the total porosity. This is due by the breakdown of carbonates at high temperatures, releasing carbon dioxide, CO_2. A fast escape of the gas from the ceramic body can lead to a high open porosity and to the so-called pinholing effect on the tile's surface. On the other hand, a slow gas breakout can result in an increased closed porosity caused by the embodiment of the bubbles inside the body. For these reasons, the use of carbonates and carbonatic clays, if considerable in the past for the production of ceramic products as *monoporosa* and *birapida*, is nowadays strongly receding (Dondi *et al.*, 1992; Dondi, Raimondo and Zanelli, 2014). However, a little percentage of these minerals is sometimes added as additive in mixtures for porcelain stoneware tiles because of their effect as sintering promoters. The same action can be likely performed through the use of talc or glass-ceramic frits.

1.2.4.3. Soluble salts

The presence and abundance of soluble salts is another import factor to assess when choosing a raw material for manufacturing ceramics. This term refers to all those carbonates, sulfates and chlorides soluble in water that are often found in clays and in sedimentary deposits. In **Table 1-4** are listed the most occurring soluble salts together with their solubility values (PubChem). The origin of these minerals is usually strongly related to precipitation and sedimentation mechanisms of fine particles in marine environments. Other sources are ascribed to the transporting action of water carried out by rivers and rains on land. The least soluble salts can often be found in vast deposits or as big crystals while others are usually homogeneously distributed within rocks and sediments.

Table 1-4. The most common soluble salts found in clays with their water solubility values measured at 20°C. (*) indicates values measured at 25°C.

Salt	Water solubility (g/L) at 20°C	Salt	Water solubility (g/L) at 20 °C
$CaCO_3$	0,014*	$MgCO_3$	0,10
CaCl	745	MgCl	543
$Ca(OH)_2$	1,7	$Mg(OH)_2$	0,009
$CaSO_4\ 2H_2O$	2,4*	$MgSO_4$	360
$CaSO_4$	2	$BaCl_2$	370*
NaCl	360*	KCl	355*
Na_2CO_3	307	K_2CO_3	1110*
Na_2SO_4	445*	K_2SO_4	111*

Thus, the presence of soluble salts in raw materials for ceramics is quite a constant and, for this same reason, it has to be taken under strict control. For example, these minerals have a non-negligible role on the rheological behavior of ceramic suspensions. In this regard, they can act on the viscosity and also rouse flocculation events. Usually, high charge cations as Fe^{3+}, Ti^{3+} or even Ca^{2+} and Mg^{2+} have a detrimental effect on clay particles stability, while monovalent ions as Na^{+} and K^{+} display the opposite action (Società Ceramica Italiana, 1984).

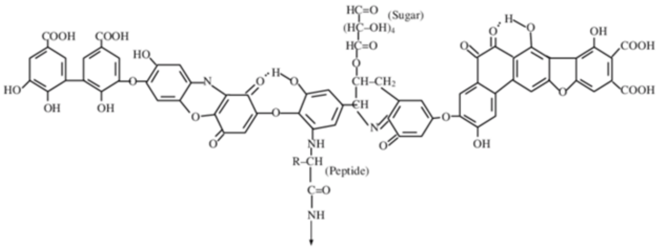
Other problems are involved during firing because of the tendency for soluble salts to go through pyrolysis or dehydration once exposed at the high temperatures of this stage. Here, CO_2, SO_3 and H_2O gasses are released by carbonates, sulfates and hydroxides, respectively. As mentioned before, an uncontrolled gas breakout can lead to imperfections on the tile's surface and to the so-called pinholing effect (SACMI, 2001). This is even more critical in single-firing products as porcelain stoneware. In addition, as it will be thoroughly treated in the following chapters, CO_2 and SO_3 related emissions have a strong impact on the environment according to the greenhouse gas nature of the first species and to the extreme reactivity and acidic behavior of the second. However, one of the most problematic consequences related to the presence of soluble salts is represented by the efflorescence phenomena (Parisotto *et al.*, 2021). The term indicates the residues of mineral left on the tile's surface after heating processes as firing or drying or ensuing by the action of humidity during time. All those factors promoting the migration of salts inside the fired body, as the higher number and dimension of pores, contributes to the intensification of this phenomenon. Besides the obvious aesthetic damages generated in unglazed tiles, an extensive efflorescence can lead to an improper firing of glazes. In fact, an excessive and heterogeneous concentration of salts is the cause of the uneven fusibility of frits and glazes, as a consequence of their chemical alterations. Fortunately, the low water absorption values for porcelain stoneware are one of the granting factors for a low incidence of efflorescence during time. Regarding the other causes, as the changes in firing parameters are often impractical or ineffective, the best solution to avoid such events still remains the adoption of raw materials containing limited amounts of soluble salts.

1.2.4.4. Sulfides

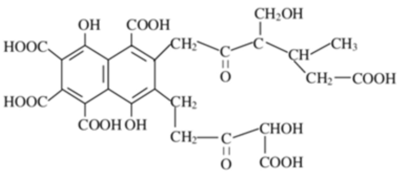
Along with some of the sulfates mentioned above, there are also other minerals containing sulfur often found as impurity in raw materials for the ceramic industry. Among these, the most occurring ones are pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and alunite ($KAl_3(SO_4)_2(OH)_6$). Some feldspathic or clay raw materials coming from volcanic areas can also exhibit different amounts of native sulfur (S_8). This element has always a detrimental effect, mainly because of its conversion in the hazardous SO_2 and SO_3 gasses at high temperatures. The oxidation reactions of sulfur are responsible for the deterioration of kiln's walls and a source for environmental pollution (Timellini, Resca and Bignozzi, 2016). Besides, the release of gas causes volume expansions, leading in turn to micro cracking inside the ceramic body. An extensive occurrence of these defects is one of the main reasons for modest mechanical properties as, for examples, a low flexural strength. Sulphur can also act as a reducing agent for iron (III) during firing, contributing in such manner for the appearance of the black-core effect, particularly evident in fast-firing products as it is the case for porcelain stoneware tiles (Corradi *et al.*, 1996).

1.2.4.5. Organic matter

The raw materials for ceramic manufacture most rich in organic matter are certainly clays, because of their sedimentary origins. Among the soil components acting as impurity, there are microorganism and organic compounds synthesized by them, together with plants and animal detritus at various stage of decomposition. These latter account for humus, a dark organic matter composed by fulvic acids and humic acids, which chemistry have not yet been fully understood. However, possible structures for these molecules have been hypothesized since years (**Figure 1-13**).



(a) Humic Acid (Stevenson 1982)



(b) Fulvic Acid (Buffle 1977)

Figure 1-13. Two hypothetical model structure for a humic acid and a fulvic acid (Buffle, 1977; Stevenson, 1982).

In this manner, clays can display relatively high percentages of nitrogen, phosphorus and, obviously, carbon. All the relative chemical species contributes to the so-called *loss on ignition* (LOI), which accounts for the loss of weight after the burning process of a sample of material at 600 °C, in the case of organic matter determination. In the ceramic science, the LOI is strongly indicative of the tendency of a material to release gasses during the firing process. In addition, the presence of carboxylate and phenolate groups in the structure of the above-mentioned acids, allows the binding of metal ions as Mg^{2+}, Ca^{2+} and Fe^{3+}, which have been proved to have an effect on the rheological behavior of ceramic suspensions (Società Ceramica Italiana, 1984).

The organic matter inside a ceramic body is the primary cause for the so-called *black-core* effect, often observed in ceramic products after firing. In particular, this problem has a high recurrence in the production of porcelain stoneware tiles, being responsible for a lower quality of products and strongly affecting in this way their market.

The decomposition of the organic substances starts around to 250 °C inside the kiln, with the consequent release of H_2, CO and CO_2 gasses (SACMI, 2001). However, an increased number of pyrolysis events takes place in the inner layer of the tile with the increasing temperature because of the lower oxygen content in this region. At this point, the burnup rate of the carbonaceous residue is regulated by the oxygen diffusion through the ceramic layer. The oxidation is then carried out through the following reactions:

$$C + O_2 \leftrightarrow CO_2$$

$$2C + O_2 \leftrightarrow 2CO$$

The presence of incandescent coal together with a deficiency in oxygen lead to high carbon monoxide evolution. On the other hand, the formation of the liquid phase promoted by fluxing agents at temperatures around 1000 °C contributes to isolate carbon before being fully oxidized. Carbon monoxide plays a fundamental role in the reduction of iron oxides via this set of reactions:

$$3Fe_2O_3 + CO \leftrightarrow 2Fe_3O_4 + CO_2;$$

$$Fe_3O_4 + CO \leftrightarrow 3FeO + CO_2;$$

$$FeO + CO \leftrightarrow Fe + CO_2$$

In this regard, the formation of the black core is connected to higher amount of FeO and unburned carbon in the inner layer of the tile (Moshnyakov and Abdrakhimov, 2019). The extensive use of fluxes promoting the start of sintering processes at relatively low temperatures and the extremely short firing time displayed by porcelain stoneware tiles, are the main causes for their high sensitivity. In particular, the short time of residence inside the kiln does not allow an effective diffusion of the oxygen through the ceramic body, leading in this way to all the above-mentioned processes. It is worth highlighting here, as the black core effect more easily occurs in ceramic tiles characterized by high thicknesses (2 or 3 cm). In fact, the higher depth that gasses must reach to promote oxidation mechanisms hinders such processes.

The presence of unburned carbon during firing can also cause other defects as swellings, cracks or black spots. These latter are due to the carbonization of macroscopic residues of organic matter. As well as for black core, the occurrence of these events will increase with the increasing thickness of the tile. In theory, all these problems could be eliminated through holding the article for a certain time at a temperature where the rate of carbon oxidation is still high while the liquid phase has not yet been formed. However, such solutions are not always practically or economically favorable. The easiest way still remains the adoption of raw materials characterized by a low content of iron oxides and organic matter.

In some documented cases, the elimination of the presently mentioned impurities in clays has been accomplished by means of physical or thermal treatments with positive outcomes as, for example, the wet sieve method, the hydro-cycloning method and the electromagnetic filtering method (Barrachina *et al.*, 2017). Nonetheless, because of the economic impact of these methods, their feasibility strongly relies on clays that needs to be far less expensive than others characterized by higher purity.

1.2.4.6. Additives

Additives are special chemical compounds, rarely natural raw materials, which are added to ceramic formulations or glaze suspensions principally to improve rheological behavior. The nature and exact amount of such ingredients is usually kept secret by companies. Thus, it is difficult to find full descriptions of additives used in ceramic production from the scientific literature and the know-how is jealousy retained by ceramists or by additives companies. However, the main adopted additives are known, and their use largely consolidated.

Additives are mainly employed as dispersants, deflocculants, plasticizers or to perform a bactericidal action.

When dealing with ceramic batches, the most adopted additives is the class of polyphosphates, exhibiting a fluidifying and deflocculant action. These salts act by chelating polyvalent ions reducing flocculation events and, thus, reducing viscosity of ceramic suspensions. As an example, sodium polyphosphate is particularly employed, up to 0.2-0.4 % on weight in ceramic suspensions. Other used additives are the ammonium or sodium polyacrylates, performing a strong fluidifying action which makes this class of deflocculant more effective if compared to polyphosphates. However, the organic nature of polyacrylates is responsible for the emission of volatile organic compounds (VOCs) which negatively affect the environmental impact during the firing stage.

On the other hand, when dealing with glaze suspensions, the quantity and nature of additives slightly differ. Among these, sodium chloride is used in low quantities, to 0.1 to 0.3% to increase the viscosity of glazes while some clays and kaolin are employed with the same purpose but in more consistent quantities, up to 2-4% on weight. Another important additive is the carboxy-methyl-cellulose (CMC), employed at variable percentages, from 0.6 to 2% or more, which are able to lower flocculation events and to improve cohesion with the ceramic support during glaze deposition (SACMI, 2001).

1.2.5. Raw materials for glazes and engobes

The raw materials involved in the formulation of ceramic glazes and engobes for porcelain stoneware tiles comprise most of the ones above illustrated for the ceramic body, with the addition of a supplementary number of minerals and oxides. However, it is highlighted here as both glazes and engobes are normally produced from third parties and ceramic tile factories limit the manipulation of these materials only to the production of suspensions and to application. In fact, they are transported inside productive plants in big fabric bags, under the form of powder or granules. Then, in order to avoid an excessive agitation time which can have a detrimental effect on the properties of suspensions, these are prepared just before use. The content of the fabric bags is thus purged inside Aisling mills of appropriate dimensions with fresh water, and, after the right agitation time, suspensions are sent to decoration units ready to be applied on tiles surface.

As a consequence, the description furnished in the following sections for the raw materials for glazes and engobes is not to be considered an exhaustive picture of all the materials involved in this sector.

1.2.5.1. Glazes

The main raw materials associated with the production of glazes are synthetic materials called *frits*. These are semi-finished products obtained through melting of specific mixes of minerals and oxides inside rotative kilns at temperatures around 1400-1500 °C. Once the melt is obtained, it is poured inside water yielding a solid mass which is finally crushed in pellets and stored in big fabric bags. Frits are very similar to glasses, with the difference that are not perfectly homogenized and amorphous materials but presenting residual crystalline phases and air bubbles to various extent. The objectives of this working phase are various. In particular, there is the necessity of trapping inside a glassy matrix some components that will be otherwise solubilized once in contact with water during the preparation of the glaze suspension. Additionally, the high temperatures grant the complete elimination of organic impurities, the dispersion of the presence of little aggregates of iron or other metallic species all over the mass of the frit and, most of all, favor the development of new phases that will be otherwise forming during the firing of ceramic tiles.

Frits are generally employed in ceramic glazes up to 90-95%, together with minor additions of ball-clays or kaolin, up to 5-10%, to improve rheology and contact with the ceramic support, and some additives tailoring the properties of suspension as viscosity and homogeneity.

Raw materials for frits preparation are quartz and sands, sodic or potassic feldspars, boric acid (H_3BO_3), alumina (Al_2O_3), calcium carbonate and dolomite ($CaMg(CO_3)_2$) , zircon silicate ($ZrSiO_4$), zinc oxide and barium carbonate ($BaCO_3$).

Among the components, silica is the most important, representing the principal constituent of the glassy matrix. Glazes rich in silica possess a high resistance to chemical agents and a high hardness. However, increasing the content of silica results in the increase in firing temperature of the glaze. For this reason, melting temperatures are generally reduced by the presence of sodium or potassium oxides (Na_2O and K_2O), contained inside corresponding sodium and potassium feldspars. In the past, lead oxide (PbO) was used for its fluxing action and as modifier of the glassy reticule, able to increase the index of refraction and gloss of glazes. Nowadays, the use of lead is strongly inhibited by the strict character of regulations in terms of atmospheric emissions and leaching of heavy metals from ceramic surfaces and from ceramic wastes. Its role has been substituted by boron, introduced through boric acid. Calcium oxide increases phase stability of frits and improve mechanical hardness of glazes and adhesion to the ceramic support. Alumina helps controlling the coefficient of thermal expansion in glazes and improves opacity and resistance to chemical attack. Finally, zircon silicate is introduced by virtue of its great opacifying action and its high level of white. Inside frits, zircon silicate remains mostly under the form of crystals dispersed inside the glassy matrix because of its high melting temperature. Another important action carried out by this component is to contribute in the stabilization of the coefficient of thermal expansion of glazes, reducing in this manner the occurrence of cracking events after the firing stage of ceramic tiles.

1.2.5.2. Engobes

Engobes are somewhat in between the ceramic body and glazes, having in common with them the raw materials involved in their production. Engobes for porcelain stoneware tiles are normally composed by a frit portion, ranging from 20 to 40% on weight in the formulations, by one or more ball-clays and by feldspars, quartz and zircon silicate. The function of frits is essentially the formation of the glassy matrix while clays are responsible for the necessary plastic characteristics. Feldspars and quartz are employed to set fusibility and thermal properties to proper values while zircon silicate is added to improve hardness and total whiteness of the engobe, contrasting the darkening effect of clays. Another function of zircon silicate is to tune the coefficient of thermal expansion (CTE) of the engobe to grant a proper matching between the ceramic body underneath and the upper glaze layer.

1.3. The production process of ceramic tiles

Ceramics have been produced since centuries almost all over the world, spanning from simple utensils to great art masterpieces. However, the evolution in the production processes have always been advancing by little steps over time. In the past, the manufacture was strongly linked to the nature and amount of natural resources available near the productive points, confining in this way the investments and preventing the exchange of technology and information between producers. However, during the twentieth century, the ceramic tile sectors, especially the Italian one, experimented an intensive mechanization of the production processes and a concomitant refinement of the quality of raw materials. Furthermore, the introduction of the fast-firing technique was able to reduce the costs and times of the process to a great extent. This led to a sort of industrial revolution that ended up in the late seventies with the introduction on the market of porcelain stoneware. This new product accounted for an almost complete innovation of the production process of ceramic tiles (Sánchez *et al.*, 2010). The most important innovations were the introduction of the wet grinding route and the connected atomization technology and the incredible progresses in the surface decoration process.

In the following section, a typical production process for porcelain stoneware tiles will be described taking as example the reality of the Italian ceramic sector. A general representation is provided by **Figure 1-14**, which shows the complete production cycle that will be outlined below in each specific step.

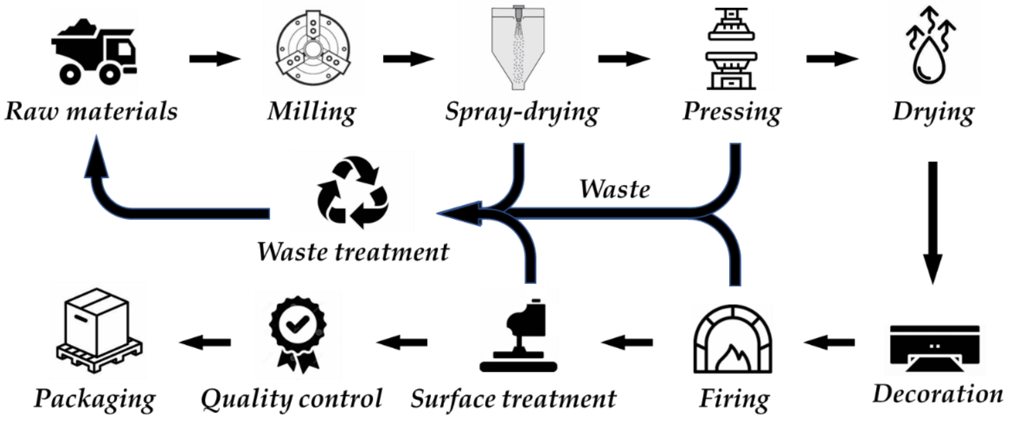


Figure 1-14. Schematization of the industrial production process of ceramic tiles.

The production process of ceramic tile starts with the arrival of the raw materials from the extraction point. The transportation is usually carried out on land by train and truck or, especially in the case of Ukrainian clays and Turkish albitites, on water by ships (Dondi *et al.*, 2021). Clays, sands, feldspathic rocks and other materials are then stored in roof-covered warehouses where they are moved by scrapers. Here, according to a specific formulation, all different raw materials are weighted and transported to the milling phase through conveyor belts.

Historically, the milling stage has always been carried out through the dry route. Such technique involves the mechanical disintegration of raw materials without the use of dispersing agents. It usually takes place inside multiple ball mills stored in a closed and separated environment because of the high dust evolution. Nowadays, this milling technology is far less employed, being limited only to special products like *majolica* and *bicottura*. On the contrary, the election technique for the milling phase is the wet route, designed specifically for porcelain stoneware. In this case, the milling is performed using water as a dispersing agent and with the use of deflocculants in order to prevent aggregation phenomena and to limit the amount of water. This technique is able to purse a mean granulometry of particles of 17-20 μm with a perfect homogenization of the different materials in the liquid medium, producing a ceramic slurry known as "*barbottina*", characterized by a density around 1,7 g/cm^3. As illustrated in **Figure 1-15**, mills are represented by massive metallic cylinders fixed to the ground and rotating on their axis in a continuously working condition through an engine device. The inner surface of the mill is coated with a tough material of the same nature of the grinding medium, represented spheres characterized by different diameters. The materials usually employed for this scope are silica (SiO_2) or alumina (Al_2O_3).

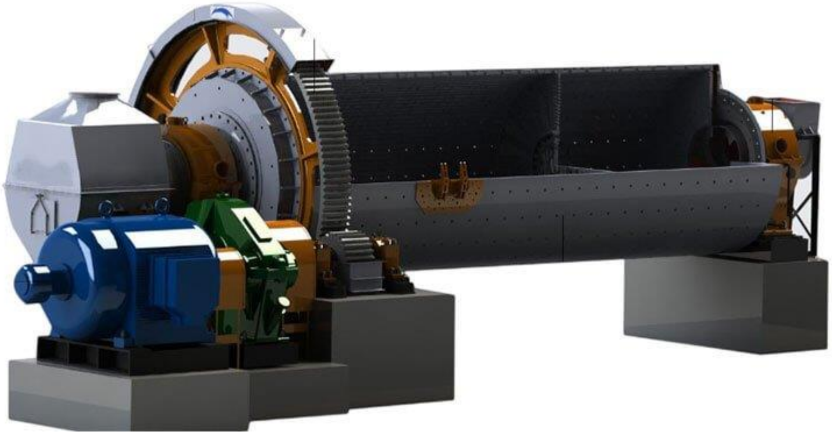


Figure 1-15. Representation of a ceramic wet ball mill, from (Mancy, 2020).

The mill is filled almost till its half capacity with the spheres, water and the raw materials to be grinded. The true capacity of the commonly employed mills ranges from 30.000 to 150.000 liters. The most important factors ruling the outcome of the grinding phase are the rotating speed, the overall extent of charging and the corresponding ratio between the grinding spheres and the raw materials.

At the end of this stage, the quality of the ceramic slurry is assessed by checking specific parameters as its temperature, density and viscosity. Rated positively, the slurry is extracted from the mill and stored in underground tanks. Under a continuous stirring, the slurries can be now added with particular liquid dyes for the production of colored porcelain stoneware bodies or, differently, moved directly toward the spray drying stage.

The spray-dry technology has been used for years in other manufacturing fields as the pharmaceutical and feeding industry. It was introduced in the ceramic production process as a result of the adoption of the wet milling route. This technique allows the obtainment of a round shaped ceramic granules characterized by a well-defined granulometry and a controlled humidity, normally around 5-6%. The following shaping stage, in fact, is strongly affected by these latter aspects of the particles. Besides, the handling and storage of the ceramic powders has been made far more practical with the introduction of a spherical shape if compared to the old dry milling route, where the particles presented widely disparate profile and sharp contours.
A spray-dryer has a great cylindric chamber with outer aluminum wall and the inner zone, where hot air is let circulating at a temperature of 500-600 °C, cladded with stainless steel and insulating material (**Figure 1-16**).

Figure 1-16. Photograph of a ceramic spray-dryer inside a ceramic factory, from (Spray Driers).

The ceramic slurry is pumped from the stirring tanks through filters in order to prevent the occlusion of the nozzles inside the spray-dryer. Then, it runs towards a dispersing ring mounted with nozzles and here sprayed in the dryer tower. The liquid particles move onto the hot air flux losing water by evaporation until they precipitate to the bottom of the spray-dryer. Here, they are discharged over conveyor belts toward the storing silos. During the drying stage, the powder particles are formed with a peculiar holed-sphere shape after the evaporating and compacting phenomena. The statistical distribution of the spray dried granules ranges around 300-400 μm. Bigger particles are likely to form aggregates because of the higher level of residual humidity, while particles with diameters lower than 70 μm are going to be blown out toward the chimney.

The spray-dried powder is then extracted from the storing silos and transported to the shaping devices. The pressing phase allows the compacting of the granules with a contemporary reduction in the voids between particles and an increase in the density of the product. In order to obtain a crude tile exhibiting a sufficient strength for the following handling and working operations, the parameters of this phase must be rigorously tuned. Amongst these factors, there are the homogeneity in the filling of the die, the humidity of the powder and the shaping pressure. As long as ever more larger tiles are designed, the sensitivity of the pressing operation become increasingly difficult to deal with. For this reason, alternative shaping methods are being introduced. For large ceramic slabs, for examples, the continuous pressing technology with rotating cylinders is a common choice. However, almost the entirety of the porcelain stoneware tiles produced in Italy adopts the pressing technique.

The level of open porosity reached after the shaping phase will have a crucial role during the firing stage. In fact, it must be both sufficiently low, in favor of an optimum sintering, and high enough for a good permeability from gasses, granting in this way a fundamental gaseous exchange with the atmosphere inside the kiln (Amorós *et al.*, 2007).

Immediately after the press, the crude tiles go through the drying stage, that can be achieved in vertical or horizontal dryers. This process aims at eliminating the residual humidity from the product, in order to ease its handling and the decorating operations and to limit the shrinkage in firing. Inside the dryer the tiles encounter a flux of hot air at a temperature of 100-120 °C with an initially quite high level of humidity, afterward decreasing. In fact, the crude tile needs to be previously warmed to avoid an excessive surface evaporation. After that, the capillary diffusion of the water from the inner zones leads the drying stage. The dried tiles at the end of this stage can be transported through the decorating unit or directly into the kilns.

The design and production of glazes and frits is not pursued inside a ceramic factory and those products are bought directly from the manufacturer as solid powders or in flakes. Inside the plant, glazes are prepared through wet milling near the storehouse and often during the night, limiting in this way transports and energy use. The Alsing type mills used for this aim have a true capacity of near 5.000 liters and the inner walls cladded with alumina in order to prevent possible adulterations of the glaze. After the milling, the liquid glaze is stored in stirring tanks and it can be transported from here to the glazing unit. Usually, the storing time is limited because of the possibility of hydrolysis mechanisms or bacterial contaminations.

Before the application of any glazes, the surface of the dried tiles is often covered with a thin layer of an engobe. This is a ceramic-type coating able to reduce degasification phenomena from the body and to enhance its impermeabilization. It is also used to reduce the negative effect of the often-dark tones of ceramic bodies on the aesthetical appearance of digital decorations on the surface of tiles. Furthermore, its application allows a better outcome of the firing stage and limits the possible onset of aesthetic flaws, through the matching of the coefficients of thermal expansions (CTE) of the glaze and the ceramic body (Peterson *et al.*, 2007). In fact, an improper match of the thermal properties of the layers will probably result in crazing or peeling effects, as surface problems, or in a convex or concave warping of the whole tile.

In the past, the most common techniques in use in ceramic decoration were the serigraphy and the roller printing while, nowadays, the most employed method in the production of porcelain stoneware tiles is the ink-jet digital printing. It is a contactless printing technique, which has rapidly gained the market also thanks to the obvious advantages linked to the absence of screens and rollers that had to be replaced every time the image or tone changed. In the case of digital printing, a software drives the printer and manages the graphics at the same time. The ink, generally a ceramic pigment in suspension in organic media or, more rarely in water, is directly laid on the surface of the tile through a drop-on-demand technology, where droplets of ink are produced only when required (Gardini *et al.*, 2008, 2015). Such technology allows an incredibly vast set of images, tones and effects that will be otherwise impossible to reproduce through serigraphy or roller printing. It was, in fact, possible to recreate the same aesthetical appearance of other covering solutions as wood, marble, metals and concrete, by virtue of the high obtainable resolution (**Figure 1-17**). This is certainly one of the main reasons that boosted porcelain stoneware tiles production over the years.

Figure 1-17. Photograph of a porcelain stoneware tile decorated with a marble effect through ink-jet digital printing.

The most important and critical step of the whole production of ceramic tiles is the firing stage. This process must be accurately designed according to the thermal behavior of a specific ceramic formulation and the size of the tiles. In fact, because of all the physical and chemical reactions taking place during firing, this stage is particularly sensitive with a wide range of defects possibly occurring in the finished product. Usually, a vitrification plot is set up in order to study the firing stage. Here, the shrinkage and the water absorption are plotted against the firing temperature. Thereby, the maximum of the heating curve will be established upon the optimum values of these parameters. Porcelain stoneware tiles are normally fired at maximum temperatures ranging from 1150 to 1250 °C, in firing cycles spanning from 35 to 80 minutes, depending on composition of the ceramic formulation. The rest of the curve, as well as the cooling phase, will be modeled according to the most critical events arising inside the ceramic body. In **Table 1-5** the principal ones are shown.

Table 1-5. Schematic representation of the principal thermal events occurring during the firing stage of a porcelain stoneware tiles.

Temperature (°C)	Event
100	elimination of hygroscopic water
200	elimination of zeolitic water
350-650	combustion of the organic substance and dissociation of mineral sulphides (as FeS)
450-650	elimination of constitution water and destruction of the crystalline reticule
573	allotropic transformation of quartz α→β with a harsh volume increase
800-950	decarbonation of calcite and dolomite
>700	formation of new crystalline phases
900	thermal dissociation of sulphates and fluorides
>1000	possible evaporation of some alcaline oxides, lead oxides, zinc oxides and others

However, the exact temperature of each specific transformation is strongly related to the nature of the raw materials employed and to other technological features of the dried tile, as its compactness, its dimensions and the residual content of water (Martín-Márquez *et al.*, 2009). For this reason, kilns are designed in order to allow the modification of the heating curve for a specific ceramic product. There are a lot of parameters to play on in this regard. For example, the oxidizing or reducing nature of the atmosphere inside the kiln and the relative pressure of the gasses.

Nonetheless, even if with different temperature gradients and times, usually firing stages show a similar trend. A ceramic kiln is generally built with an insulating masonry and mortar structure coated with insulating fibers and, externally, by metal panels. On the inside, a monolayer series of alumina tubes stretches on its entire length, which can reach several tens of meters, even up to 120 meters (SACMI, 2001). Methane is almost everywhere used as the election fuel, while far less used are light oils as kerosene and naphtha. In fact, methane displays low cost, low level of CO_2 emissions and low sulfur impurities, if compared to other fuels.

The kiln can be divided in different heating modules, each one with a specific purpose: the warming, the pre-heating, the firing, the fast-cooling, the slow-cooling and the final cooling zones (**Figure 1-18**).

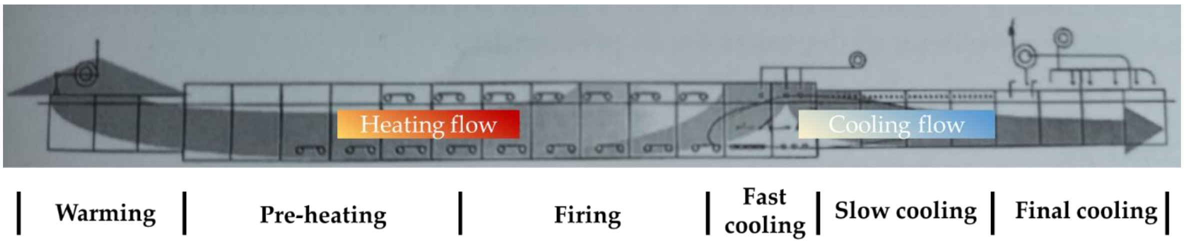


Figure 1-18. Schematic representation of the air flows and heating and cooling zones inside a kiln designed for ceramic tiles.

At the entrance of the kiln, in the warming zone, the air stream coming from the heating zone is responsible for the evaporation of residual water in the ceramic tiles. Then, the pre-heating zone is responsible for all those reaction releasing gasses which must be removed from the ceramic body in order to avoid drawbacks after the melting is reached. It is in the firing zone that tile undergoes to partial melting and events of viscous flow start enacting. Air is pumped previously heated in the firing zone in order to pursue an energetic optimization. In fact, the adoption of air from the cooling zone, at 230-250 °C , as a comburent, reduce the gas consumption up to 12-14% (SACMI, 2001).

The combustion gasses developed in this zone are then transported counterflow toward the advancing material granting a pre-heating treatment and an additional energy saving. Afterwards, fired tiles are rapidly cooled in the fast-cooling zone through streams of cold air fanned both over and under the layer of the alumina tubes. Around a temperature of the pieces of near 600-700 °C the cooling rate is decreased in order to provide time for the allotropic transformation quartz $\beta \rightarrow$ quartz α, which can safely proceed in the slow-cooling zone. After this point, the cooling is completed, and the temperature of the pieces is lowered till manageable values. From this moment on, all the working phases are no longer able to modify the technological characteristics of the ceramic product.

Other important stages of the production process of ceramic tiles, not always necessary but ever more often pursued, are the cutting, squaring and smoothing operations. Thus, tiles are cut in different shapes and squared with sharp and clear edges and according to precise calibers. In addition, in order to yield a top-quality product, the porcelain stoneware tiles undergo to further mechanical treatments for the enhancement of the aesthetic aspect of the surface. The lapping, the smoothing and the polishing operations use rotating discs mounted with diamond granules with various granulometry that are able to eliminate the asperities of the ceramic surface. In this manner, tiles are presented with a satisfying smooth and shiny appearance significantly boosting their final aesthetic. In this operating unit, there are a series of different automated tools working sequentially over each single tile. Here, human activity is only limited to parameters setting and supervision.
All mentioned machineries adopt high quantities of water as cooling fluid and, also, as dust trap. However, the wastewater ensuing from such operations is not discharged but transported to deposition tanks where ceramic particles are separated from water after sedimentation mechanisms. In this manner, the two materials can efficiently be reinserted in the production process with basically any loss.

Before going through final operations, tiles are directed to the quality division where are checked for color or physical defects and are divided into classes according to quality parameters relating to color, caliber accuracy and defects. Typically, first quality tiles are labeled and sent directly to the market while lower quality products can be sold under more economical brands, marketed for other uses or, eventually, sent to granulation for recycling purposes. Actually, the just mentioned stage of the process can sometimes be performed in advance to mechanical treatments in order to deliver to such operations only the first quality pieces or, else, to direct different qualities of tiles to different treatments. In this case, the sequence of these steps is not fixed and may vary from factory to factory.

The final stage of the production process of ceramic tiles takes place in the packing and storage units. A whole automated arrangement of different mechanical devices gathers tiles according to a specific quality class and pack them with a protective carboard envelope. There is not a specific number of pieces in a pack. Large formats, as 90x90 cm tiles, are usually packed in pairs. Medium formats, as the 60x60 cm, are usually grouped from 2 to 6, while lower ones, as a 30x30 cm format, can be packed in higher numbers, of 10 or more. Finally, thickened tiles or large slabs, as 120x240 or 240x320 cm formats, can even be wrapped singularly. At this point, the sets of tiles are piled together over wood pallets granting the best optimization of the space. Each pallet is covered with a thermoplastic envelope in order to protect the lot from the weather conditions and then banked in the outdoor storehouse. Otherwise, lots are loaded on lorries and exit the production site toward the selling points.

1.4. Emission control techniques

In this section, a focus is made on the strategies and techniques adopted within Italian ceramic tile factories to control and prevent atmospheric emissions coming from the production processes.

Each operation along the manufacturing line is related to an emission point, usually a chimney, connecting the inner working process with the external environment. Thus, if not properly contained, pollutants can escape into the atmosphere, resulting in possible hazards for humans and nature. In **Table 1-6** are reported the main pollutants for each of the emission point of the production process of ceramic tiles.

Table 1-6. Main pollutants related to principal working operations of the production process of ceramic tiles. Concentration levels refer to the relative amount of pollutant respect to the most polluting operation. PM: particulate matter; VOC: volatile organic compounds; SiO_2: crystalline silica; Met.: heavy metals.

Operation	PM	F	Cl	NO_X	SO_X	CO	CO_2	VOCs	SiO_2	B	Met.
Raw materials storage	•								•		
Wet milling	•								•		
Dry milling	•••								•••		
Spray-drying	••	•	•	•		••	••		••		
Shaping (pressing)	••								••		
Drying	•			•			•		•		
Glaze preparation	•								•	•	•
Decoration	•							•	•	•	•
Firing		•/••	•/••	••	••		•••	••	•	•	•
Post-firing operations	•								•		
Packing								•/••			

• : low; •• : medium; ••• : high

As it can be seen, the main pollutant of the whole process is the particulate matter, which is found in basically all emission points, with the exception of the firing step and packaging procedures. The production of ceramic tiles, in fact, is based on a powder technology and, even if during last decades the concentration of these two pollutants has been incredibly lowered, a complete containment of particulate matter from the manufacturing lines is almost impossible (Boschi *et al.*, 2020). The SiO_2 represents the crystalline silica fraction inside the particulate matter, to which is usually found associated, even if in a far lower amount. Its presence inside working environment can imply serious consequences for the health of workers, if exceeding the precautionary limits. The respirable fraction of crystalline silica (with a median diameter of 4.25 μm and a maximum limit of 10 μm, according to *BS EN 481:1993*), in fact, is responsible for silicosis, an inflammatory lung disease which became famous in the past all over the world when it was recognized as occupational disease after the high number of cases registered, introducing the discussion regarding safety in the workplace (Plant, Voulvoulis and Ragnarsdottir, 2012). However, most dusty operations as the dry milling, have been almost totally replace by the safer wet milling procedure. Likewise, the particulate matter, if not properly contained, can negatively affect the salubrity of working environments and, when entering into the atmosphere, it contributes to the average concentration of atmospheric $PM_{2.5}$ and PM_{10}.

The equipment responsible for the abatement of particulate matter are usually fabric filters or cyclones. The first ones use fabric cylinders to trap the particles when the air flow is letting through the channel of the cylinder. Then, the layer of powder particles is released in a bag below the filter by using a counter-flow air stream at high pressure. Cyclones, on the other hand, use circular air streams to direct the particles on the wall of the equipment by harnessing the centrifugal force. Falling by gravity, the powder is then collected in a beg below the filter.

Among the most characteristic pollutants connected to the manufacturing of ceramic, there are the compounds of fluorine and chlorine, especially hydrofluoric (HF) and hydrochloric (HCl) acids, and other related compounds. These chemical species are formed after the collapse of the clay structure during firing, when fluorine (F^-) and chlorine ions (Cl^-) are released from the crystalline reticule and let free to react with the environment (Bonvicini, Fregni and Palmonari, 2006; Monfort *et al.*, 2008). As an example, the reaction with water molecules delivers the corresponding acidic species, HF and HCl. These compounds represent a serious hazard of acidification of the ecosystems near industrial installations and, especially fluorine related species, can result extremely toxic for the human health.

The release of fluorine from the clay structure starts from 800 °C and continues up to peak temperatures. Even if sometimes it can be found in flue gas from spray-drying operations, the presence of this pollutant from such emissions is usually very low to the point that not all environmental authorizations require its monitoring at spray-dryers.

The abatement of fluorine and chlorine compounds inside flue gas from kilns is carried out by chemical action of calcium hydroxide ($Ca(OH)_2$) within fabric filters. The gas flow is let passing through fabric cylinders charged with calcium hydroxide powder adsorbing the gaseous compounds and promoting the following reaction:

$$Ca(OH)_2 + 2HX \rightleftarrows CaX_2 + 2H_2O$$

Where X can be F^-, Cl^- or $\frac{1}{2}SO_4^{2-}$.

Maintaining the $\frac{Ca(OH)_2}{HX}$ ratio greater than 1 guarantees a proper efficiency of abatement and grants the almost complete elimination of these pollutants from the air emissions (Busani, Palmonari and Timellini, 1995). The exhausted lime is, then, collected in bags under the cleaning plants and disposed of accordingly to its labeling as hazardous waste. Other solutions to trap and reduce acidic gases include the utilization of sodium bicarbonate ($NaHCO_3$) or mixtures of basic reagents even if, in Italy, calcium hydroxide is the most used solution.

Other gaseous pollutants related to high temperatures operations are nitrogen oxides (NO_x) and sulfur oxides (SO_x). These chemical species are not characteristic of ceramic production but, rather, of combustion processes which, along the manufacturing line of ceramic products, are regularly encountered.

Even if often jointly treated, the genesis of nitrogen and sulfur oxides is not related. In fact, nitrogen oxides are produces from the combustion reaction, where the atmospheric nitrogen is oxidized into reactive species and then transformed into stable oxides. On the other hand, sulfur oxides are generated after oxidation reactions on sulfur impurities contained in the raw materials. In the past, another possible source of sulfur were the employed petroleum-derived fuels, but nowadays the entirety of Italian ceramic tile factories is using natural gas as combustion fuel, which is naturally free from sulfur.

However, both these groups of compounds represents a serious hazard to acidification and negatively contributes to atmospheric pollution through a series of cascade reactions taking place into the atmosphere involving other reactive species as ozone (O_3), volatile organic compounds (VOCs) or hydroxyl radicals (OH) (Seinfeld, 2015).

The abatement and control of nitrogen and sulfur oxides is more difficult because, especially for NO_x, there are not economically feasible practices to trap and contain these species. The concentration of SO_x can be slightly reduced by calcium hydroxide whenever the sulfur species had reacted with water, forming the corresponding sulfuric acid, which can be neutralized by the base inside the filters. However, the only way to eliminate sulfur oxides from the atmospheric emissions is to realize a selection of raw materials with very low quantities of sulfur impurities.

Conversely, the best manner to reduce emissions of nitrogen oxides is to properly tune the fuel/air ratio in order to perform the most efficient combustion process, thus avoiding undesired side reactions.

Another class of pollutants related to firing is represented by VOCs, or volatile organic compounds. As the name suggests, VOCs are organic compounds characterized by a low molecular mass that, after an incomplete oxidation to CO_2, are released at the emissions from kilns and do not settle to ground level, being otherwise transported into the atmosphere. The organic matter from which the VOCs arise can be found as impurities in clays, as dispersing medium for pigments inside ceramic inks for ink-jet decoration technologies or, finally, as additives promoting the rheology of engobes and glazes suspensions (Timellini, Resca and Bignozzi, 2016). Besides the negative role as active species in atmospheric reactions, VOCs contribute to odor emissions which, most than any other pollutant, attract complaints from the nearby communities (Busani, Palmonari and Timellini, 1995).

The abatement of these pollutants can be carried out by means of post-combustors installed at the end of flue gas conducts. The post-combustion of gasses coming from the firing stage grants the complete oxidation of all chemical species and, thus, the elimination of VOCs. However, such solution is not generally implemented because of the high related cost and the additional amount of CO_2 emissions. The only advantage, in fact, is the elimination of a class of pollutants which concentration is actually quite low in the production of porcelain stoneware tiles and other ceramic products characterized by thin layers of glazes and adopting high quality clays.

Boron and heavy metals are further pollutants related to the decoration of ceramic products, rather than to the ceramic body. In fact, boron is thoroughly used inside ceramic frits as melting agent while compounds of many heavy metals are employed in pigments inside ceramic glazes. The fluxing action of boron was once performed by lead oxide (PbO), being also able to improve the aesthetical aspect of ceramic decoration by enhancing shine of glazes. Because of its toxicity and its large employment, lead was considered one of the most hazardous heavy metals related to ceramic tile production and a strict monitoring plan was often required by environmental authorizations. Nowadays, most glazes do not contain lead compounds and more safe ingredients are used in pigments and in glazes formulations. As a result, lead has almost been eradicated from the manufacturing process of Italian ceramic tiles.

Nonetheless, pigments for modern decoration technologies, as the ink-jet printing, are often synthesized starting from heavy metals as Co, Cr, Sb, Cd, Ni and Mn, because of their peculiar and tunable coloring characteristics (Cavalcante *et al.*, 2009). In addition, natural occurring raw materials can carry variable amount of heavy metals impurities, as As, Co, Cu, V, Mn, and Cr. For these reasons, there is an increasing concern towards heavy metals, and environmental authorizations are beginning to add requirements for the monitoring of these chemical species.

Finally, carbon oxide (CO) and carbon dioxide (CO_2) are the most abundant flue gas of the entire production process of ceramic tiles. Carbon oxide is mainly generated during the combustion reaction of natural gas in atmosphere poor in oxygen, where carbon cannot achieve its maximum oxidation state. It is mainly related to emissions from spray-dryers while ceramic kilns usually involve higher oxidizing atmospheres. On the contrary, carbon dioxide is the principal waste gas arising from the firing stage, being also present at the emissions from spray-drying and drying operations. It is the main and most abundant greenhouse gas inside the atmosphere and, until now, it has never been possible to control and to reduce in amount through economically available technologies. Nowadays, there are policies and technical instruments which have been devised to contain CO_2 emissions. Besides the EU ETS, exhaustively described in **section 2.7**, carbon capture and storage installations are becoming a reality in some countries, being able to clean flue gas from industrial operations and avoid the emission of great amount of carbon dioxide into the atmosphere. However, in the Italian ceramic sector such solution has not been implemented yet.

On the other hand, the debate on more sustainable fuels is actually proceeding, mainly focusing on blue and green hydrogen, both far more environmentally sustainable solutions but certainly not economically viable in the near future. Only important investments in scientific research and innovation will reduce costs and make the most sustainable technologies affordable for the industrial practice.

1.5. International standards for ceramic tiles

In this section, the principal ISO standards regarding ceramic tiles will be presented. The International Organization for Standardization (ISO) is a non-governmental organization founded in 1947 and including 167 members, each one represented by its own national standard body. The role of ISO is to produce technical standards regarding basically any field of technology (with the only exception of electrical and electronic engineering, which are under the responsibility of the IEC, the International Electrotechnical Commission). These standards are voluntarily complied and are internationally recognized, thus helping to reduce technical barriers to trades generated by differences between national regulations and standards among countries.

1.5.1. ISO 13006:2018 Ceramic tiles – Definitions, classification, characteristics and marking

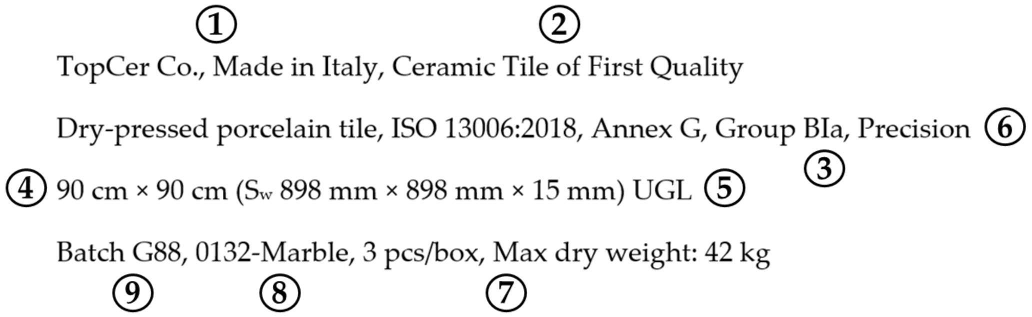
The standard *ISO 13006:2018 "Ceramic tiles — Definitions, classification, characteristics and marking*" defines the main terminology and characteristics regarding all types of ceramic tiles, providing a classification of different tiles products and a marking practice intended for commercial purpose.

The standard divides ceramic tiles into groups, according to the shaping method and the water absorption value. The assignment to a particular group is only for classification and description purposes, while not presupposing any usage of the products.

In addition to classification groups, the standard states some marking requirements and specification for ceramic tiles. In particular, the packaging of the product shall include:

1) The mark of the manufacturer and the trademark of the manufacturing country
2) The indication of first quality product
3) The classification group
4) The nominal and work sizes (S_w), namely the description size and actual size of the pieces
5) The type of surface, if glazed (GL) or unglazed (UGL)
6) Any surface treatment carried out after firing
7) The number of pieces and weight of the package
8) The color identification, as state by the manufacturer
9) The batch number

Figure 1-19 illustrates an example of the marking practice for ceramic tiles according to ISO 13006:2018, where just mentioned requirements have been pointed out.



TopCer Co., Made in Italy, Ceramic Tile of First Quality

Dry-pressed porcelain tile, ISO 13006:2018, Annex G, Group BIa, Precision

90 cm × 90 cm (S_w 898 mm × 898 mm × 15 mm) UGL

Batch G88, 0132-Marble, 3 pcs/box, Max dry weight: 42 kg

Figure 1-19. Example of mark for packaging containing ceramic tiles.

Moreover, the standard specifies a series of required characteristics for the intended use of the ceramic tile product, as internal and external wall or floor covering, together with the reference standard to carry out the testing for each specific characteristic. All standards for testing belong to the series ISO 10545.

On the other hand, explicit values regarding the dimensions, surface quality and chemical and physical properties of the classification groups are reported in the annexes section. In particular, Annex G indicates the requirements for porcelain stoneware tiles, belonging to class BI_a (*ISO 13006,* 2018). Among these, some meaningful requirements for this class are:

- Water absorption ≤ 0.5%
- Breaking strength:

for thicknesses ≥ 7.5 mm → ≥ 1300 N; for thicknesses < 7.5 mm → ≥ 700 N

- Modulus of rupture ≥ 35 N/mm^2

Furthermore, it is worth noting as the standard differentiates for some requirements between glazed and unglazed tiles. For example, the abrasion resistance is assessed following ISO 10545-6 for unglazed tiles, using the method of the deep abrasion, while for glazed tiles testing is carried out according to ISO 10545-7, employing the surface abrasion method. In this second case, the test report requires the assignment of a specific class of resistance, going from class 0 to 5, which labels the most resistant tiles. On the other hand, that does not apply to unglazed tiles, whose standard only requests to indicate the equivalent value of removed volume, without assigning any particular classification or performance rate.

A similar discrimination is made also in the case of resistance to staining agents, regulated by standard ISO 10545-14 for both glazed and unglazed tiles. However, for glazed tiles, ISO 13006:2018 sets a specific requirement of performance, that is to belong at least at class 3 on a classification from class 0 to 5, which indicates the product being the easiest to clean. Conversely, the standard does not demand any specification for unglazed tiles, while recommends consulting the manufacturer to get information on the cleaning methods.

With the technological revolution regarding surface treatments and decoration processes which have guided porcelain stoneware tiles across the last two decades, the distinction between glazed and unglazed tiles is no longer simple as before, especially for tiles with water absorption ≤ 0.5%. In particular, the thickness of the glaze layers has been reducing incredibly in certain cases, arriving at micrometric level, especially with the decoration through spray techniques. For this reason, it is possible to find ceramic tiles declared as "unglazed" even if minimal amounts of materials have actually been laid on the surface ahead the firing stage. However, it should be highlighted here that any application of additional material which is carried out before the heat treatment of ceramic tiles shall be considered equal or equivalent to glazing.

1.5.2. ISO 10545: 1-20 Ceramic tiles – Sampling and testing

ISO 10545 is a multi-part standard describing all testing procedures necessary to determine the characteristics of ceramic tiles, as presented in ISO 13006:2018. The standard is composed of 17 parts, which will be listed below and briefly described.

ISO 10545-1:2014 - Ceramic tiles — Part 1: Sampling and basis for acceptance

This standard gives indications on the sampling procedure and inspection for acceptance or rejection of a particular batch of ceramic tiles (ISO 10545-1:2014).

ISO 10545-2:2018 - Ceramic tiles – Part 2: Determination of dimensions and surface quality

This standard specifies methods for the determination of length, width, thickness, straightness of sides, rectangularity and surface flatness of tiles pieces. Measurement shall be carried out by using a micrometer screw gauge and a calibrating plate for last three features. Within the test report, measures shall be reported as individual measurements and as average value. In addition, the standard gives indication for the assessment of the surface quality of ceramic tiles. The purpose of the surface analysis is to discriminate between intentional decoration effects and surface defects as cracks, black spots, pin holes, crazing and other aesthetic and physical defects (ISO 10545-2:2018).

ISO 10545-3:2018 - Ceramic tiles — Part 3: Determination of water absorption, apparent porosity, apparent relative density and bulk density

This standard indicates the procedure for determining the water absorption and related features of ceramic tiles through the method of the vacuum chamber, specifying also the number and dimensions of the ceramic tiles to be tested. In particular, other features that can be determined in addition to water absorption are:

- Apparent porosity: expressed as a percentage (%), is the ratio between the volume of open porosity inside the tile and its total volume.
- Apparent relative density: the ratio between the mass of the sample and the impervious portion of it.
- Bulk density: the ratio between the mass of the tile specimen and its total volume (ISO 10545-3:2018).

ISO 10545-4:2019 - Ceramic tiles — Part 4: Determination of modulus of rupture and breaking strength

This standard specifies the procedure and the necessary equipment for determining the modulus of rupture and the breaking strength of ceramic tiles. In particular, it is the modulus of rupture which gives an account of the strength of a ceramic tile, by relating the breaking strength of the specimen to its minimum thickness (ISO 10545-4:2019).

ISO 10545-5:1996 - Ceramic tiles — Part 5: Determination of impact resistance by measurement of coefficient of restitution

This standard illustrates the testing method and preparation of specimens for the assessment of impact resistance of ceramic tiles by calculation of the coefficient of restitution. This property is calculated using the relative velocity of departure between the tile and a steel ball, divided by their relative velocity of approach. In the present case, the tile specimen is mounted on a concrete block by means of an epoxide resin adhesive. The coefficient of restitution gives an account of the elastic behavior of the tile, going from 0 to 1, where 1 represents a full elastic impact (ISO 10545-5:1996).

ISO 10545-6:2010 - Ceramic tiles — Part 6: Determination of resistance to deep abrasion for unglazed tiles

This standard describes the deep abrasion method for determining the surface resistance of unglazed tiles. The tile specimen is abraded using abrasive material for a specified time. Then, by calculating the length of the abrasion path, the standard provides the equivalent abraded volume by means of a conversion table. Such value shall be reported on the test report without any specification regarding a performance rate or a resistance class (ISO 10545-6:2010). The controversy related to this one and the following standards has been previously described, in the chapter describing ISO 13006:2018.

ISO 10545-7:1996 - Ceramic tiles — Part 7: Determination of resistance to surface abrasion for glazed tiles

This standard describes the surface abrasion method for determining the surface resistance of glazed tiles. In addition, it gives instructions about the number and size of specimens and the configuration of the testing apparatus. The classification of results in the test report requires the assignment of a resistance class, going from 0 to a maximum of 5. Assignment of class 5, however, compels passing the test of ISO 10545-14 regarding resistance to stains (ISO 10545-7:1996).

ISO 10545-8:1994 - Ceramic tiles — Part 8: Determination of linear thermal expansion

This standard specifies requirements for the determination of the linear thermal expansion coefficient of ceramic tiles in the temperature range from ambient temperature to 100 °C. The determination of such property gives an account of the thermal behavior of ceramic tile when subjected to temperature changes (ISO 10545-8:1994).

ISO 10545-9:2013 - Ceramic tiles — Part 9: Determination of resistance to thermal shock

This standard describes the testing method for the determination of resistance to thermal shock of ceramic tiles by alternate submission of specimens to hot (150 °C, through a heating oven) and to cold temperatures (15 °C, through a water bath). The process shall be repeated 10 times. A methylene blue solution can be used to spot pre-test defects and to highlight flaws after testing (ISO 10545-9:2013).

ISO 10545-10:2021 - Ceramic tiles — Part 10: Determination of moisture expansion

This standard describes the testing procedure for determining the moisture expansion of ceramic tiles. After having refired all specimens according to a detailed heating ramp, the initial measures for the length shall be registered and confronted with the values resulting from a boiling procedure in water. Moisture expansion is then reported as percentage from the ratio between the length change of the specimen and its initial length (ISO 10545-10:2021).

ISO 10545-11:1994 - Ceramic tiles — Part 11: Determination of crazing resistance for glazed tiles

This standard specifies the procedure for the determination of crazing resistance for glazed ceramic tiles. Crazes are fine cracks which can appear on the surface of glazed tiles caused by any mismatch between the thermal behaviors of the ceramic support and of the glaze. The specimens are submitted to hot steam and high pressure inside a pressurized chamber. After that, the surface is inspected for crazes by using a methylene blue solution (ISO 10545-11:1994).

ISO 10545-12:1995 - Ceramic tiles — Part 12: Determination of frost resistance

This standard describes the test procedure for the determination of the frost resistance for ceramic tiles intended for use in frost conditions with the presence of water. The method involve the alternate submission of specimens to frost conditions at -5 °C followed by a thawing process at +5 °C for at least one hundred times. In the test report both the final and initial water absorption values, as well as the evidence for any surface defect shall be reported (ISO 10545-12:1995).

ISO 10545-13:2016 - Ceramic tiles — Part 13: Determination of chemical resistance

This standard specifies methods for the determination of the resistance of ceramic tiles to chemical agents. The chemicals adopted in the testing are intended to resemble commonly occurring situations and stressful conditions for ceramic tiles. The specimens are placed in contact with the testing solutions for a period of twelve days, after which a visual assessment for the occurrence of any surface degradation is carried out. In the test report are then reported the classes of resistance according to the different nature of used chemicals (ISO 10545–13:2016).

ISO 10545-14:2015 - Ceramic tiles — Part 14: Determination of resistance to stains

This standard specifies methods for the determination of the resistance of ceramic tiles to staining agents. After the staining phase, a series of cleaning procedures characterized by an increasing efficacy is carried out to wipe out any leftover stain from the ceramic surface. In the test report, the tile specimen is classified on a scale from 1 to 5, based on the simplicity of the cleaning procedure, with 5 accounting for the easiest to clean surface (ISO 10545–14:2015).

ISO 10545-15:2021 - Ceramic tiles — Part 15: Determination of lead and cadmium given off by tiles

This standard specifies the testing procedure for the determination of the leaching of lead and cadmium from ceramic tiles under acidic conditions. The surface of the tile specimens are let in contact with a 4% solution of acetic acid to resemble the stressful conditions for ceramic of being in contact with acidic liquids or solutions. After the contact time, the solution is analyzed through appropriate techniques as atomic absorption or emission spectrometry. In the test report, concentration results shall be indicated both as milligrams per liter of solution and milligrams per square decimeter of tile surface (ISO 10545–15:2021).

ISO 10545-16:2010 - Ceramic tiles — Part 16: Determination of small color differences

This standard provides the testing procedure for the determination of small color differences on plain colored ceramic tiles, which should possess a uniform color on the whole surface. The test is carried out by determining the CIEL*a*b* colorimetric coordinates of alternatively a reference tile and other tiles samples. In the test report, the color difference, calculated according to standard ISO 105-J03:2009, is provided together with an agreed-on tolerance value for determining acceptability (ISO 10545–16:2010).

ISO 10545-17 - Draft

This ISO standard was a draft for the standardization method for the determination of the slip resistance of ceramic surfaces. However, it has never been published. The determination of this characteristics of ceramic tiles is currently accomplished making reference to the international standard EN 16165:2021 "Determination of slip resistance of pedestrian surfaces - Methods of evaluation"(*CSN EN 16165*, 2021).

ISO 10545-18:2022 - Ceramic tiles – Part 18: Determination of light reflectance value (LRV)

This standard specifies the test method for the determination of the light reflectance value (LVR) of ceramic tiles. LVR measures the extent of visible light reflected from surfaces when illuminated by a source of light. It is used by lighting designers to establish the type and number of light fitting needed to grant proper illumination for interior spaces. This standard is applicable to solid-colored, multicolored and non-uniform shade tile surfaces including tiles textured with different types of finishing (ISO 10545-18:2022).

ISO 10545-20:2022 - Ceramic tiles – Part 20: Determination of deflection of ceramic tiles for calculating their radius of curvature

This standard provides the testing procedure for the determination of the radius of curvature. The test involves applying a load and determining the radius corresponding to the circumference that approximates the curvature of the tile at the breaking point (ISO 10545-20:2022).

1.5.3. ISO 17889: 1-2 Ceramic tiling systems – Sustainability for ceramic tiles and installation materials

ISO 17889-1:2021 Part 1 – Specification for ceramic tiles

ISO 17889-1 marks a turning point in the construction industry by embracing sustainability expects for the individual building material, in this case, ceramic tile. It specifies sustainability requirements together with assessment methods and evaluation schemes for ceramic tiles including relevant criteria across the product life cycle from raw material through manufacturing, use and end-of-life management (ISO, 2021c). Because of its content closely related to sustainability aspects, this standard will be discussed in detail in **section 2.3**.

ISO 17889-2: Under development Part 2 – Specification for tile installation materials

ISO 17889-2 is the second part of the standard related to sustainability of ceramic tiles as construction material. It will specifically apply to tile installation materials such as adhesives, grouts and membrane. This standard is currently under development and, therefore, cannot be commented on.

2. Sustainability

2.1. Sustainable development

In first place, before introducing any discussion about sustainability in ceramic tile production, the term "sustainable" shall be defined in its original interpretation. The first adoption of the term in its present connotation dates back to 1987, when it was used in the report of the World Commission on Environment and Development, also known as *Brundtland Report* or *Our Common Future*, to define the sustainable development, that "*is the development that meets the needs of the present without compromising the ability of future generations to meet their own needs*"(World Commission on Environment and Development, 1987).

In this context, sustainability is not a science or a specific subject, rather it is an organizing principle of human activities and human development. Sustainability can be seen as the intersection point between the three existing dimensions of the global ecosystem: environment, society and economy. As illustrated in **Figure 2-1**, the exclusion of any of the three sphere implies different characters of future human development anyway excluding sustainability.

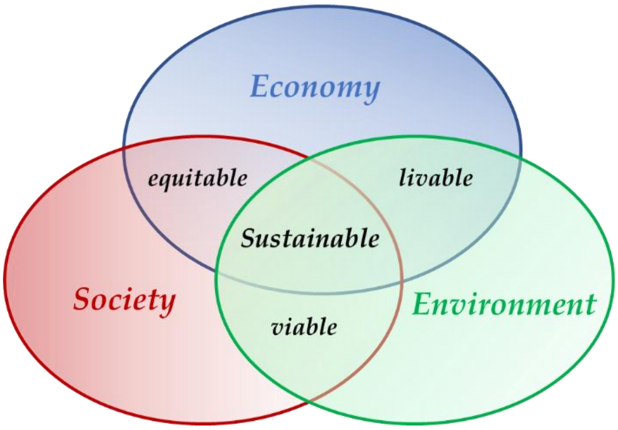


Figure 2-1. Visual representation of three dimensions of global ecosystem and of sustainable development.

Thus, equitability involves economic growth respecting human rights and social justice but does not consider environmental protection and still can contemplate exploitation of natural resources and no limits to atmospheric pollution. On the other hand, a livable development allows at the same time economic growth and conservation of natural resources but at the cost of neglecting equity in society. Finally, viable development excludes the economic dimension, leaving society defenseless into the environment without any prospect of growth. None of these outlooks for development can be sustained for long without the inevitable loss of one or more dimensions of the global human ecosystem.

It is in this context, both ahead of the Brundtland Report and after it, that many conferences have been held among world countries in order to grant a sustainable development for the upcoming future. Among the most important ones, the United Nations Conference on Environment and Development (UNCED), held in Rio de Janeiro in 1992, also known as *Earth Summit*, recognized the importance of environmental protection and the necessity to fight climate change. One of the results of the conference was the multilateral environmental agreement known as United Nations Framework Convention on Climate Change (UNFCCC) aimed at fighting "*dangerous human interference with the climate system*" and which evolved five years later in the Kyoto Protocol (*UNFCCC*). This international treaty binds signatory parties to reduction of greenhouse gases emissions through the implementation of a carbon market and of three different flexibility mechanisms, namely the International Emissions Trading (IET), the Clean Development mechanism (CDM) and Joint Implementation (JI).

Other important instruments for sustainability are the Sustainable Development Goals (SDGs), included in the United Nations resolution known as Agenda 2030, and consisting in 17 interconnected global goals dealing with environmental, social and economic aspects of sustainable development and aimed at granting "*peace and prosperity for people and the planet*" (*Home | Sustainable Development*). In this framework, industrial production can contribute to sustainability goals through the reduction of waste generation and natural resources exploitation and through a strong abatement of sources of environmental pollution. In the following sections, the waste management practices, the pollution control techniques, as well as the quality standards adopted by the Italian ceramic tile sector will be presented and discussed in the light of the work that has been and is being done toward sustainability development.

2.2. Recycled materials

As it was possible to notice in previous chapters, the number and nature of raw materials for ceramic tiles is enormous. Even if defined by three main protagonist, clay, feldspar and sand, the different genesis of such rocks and minerals has permitted the existence of an infinity of possible material assortment. Each main ingredient, in fact, can present a variety of different impurities, or be extracted with a peculiar granulometry or with a different associated humidity level.

Furthermore, the presented production process for ceramic tiles has demonstrated as there are great forces and great volumes of materials involved. In fact, various tons of natural raw materials can be processed at high pressures and temperatures, resulting in thousands of square meters of finished products per day.

Such observations suggest as the ceramic sector is particularly independent from severe technological constraints and from high purity requirements of raw materials involved. In this context, it is easy to understand as this industrial sector is one of the most advanced realities in terms of alternative raw materials and recycling perspectives. The first pioneering studies on recycling in the ceramic industry dates back to the 1970s, followed by other few examples during the 1980s and 1990s (Kats and Kvyatkovskaya, 1972; Higgins, Bauer and Carr, 1979; Abdrakhimov, Togzhanov and Saibulatov, 1990). In the same period, then, Manfredini *et al.*, 1991 published a work describing the recycling of ceramic sludges arising from the production process of ceramic tiles inside the wet grinding process for the preparation of the ceramic slip, paving the way for the future development of inner recycling policies of the ceramic sector. From that moment on, the number examples in scientific literature started growing, up to the around 300 articles on recycling in ceramics available today (Zanelli *et al.*, 2021).

However, it should be pointed out as the number of recycling strategies is certainly higher, by virtue of the vast know-how of the industrial practice and the vast numerous of existing recycling procedures actually in action inside factories, often not announced in scientific literature and rather kept as industrial secret.

Another important factor to highlight is that, if in the past recycling strategies were more driven by marketing logics, in order to increase company legitimacy or to secure green certificates, nowadays the case is substantially different. In fact, the two financial crises (2008 and 2022), together with the energetic crises and the increasing stricter requirements set by the energy transition, have lead the ceramic sector to embrace recycling strategies for economic reasons and to comply with environmental directives and regulations (*United Nations Treaty Collection*). As an example, the burst of war in

Ukraine has negatively impacted over kaolin supplying in Europe, as a cause of the increasing prices of energy and raw material itself. For these reasons, ceramic factories are increasingly adopting alternatives for exotic raw materials and solutions to reduce energetic consumptions while recycling strategies are nowadays a common reality. Various materials have been introduced inside the production process of ceramic tiles for recycling reasons. Among these and besides ceramic wastes itself, it is worth mentioning construction and demolition wastes, glass, mining residues, incinerated ashes from thermal processing of biomass, wastes from metal industry and so on. However, even if there is plenty of examples in scientific literature and even if the production process of ceramic tiles can theoretically accept numerous alternative materials, there are still some other constraints that sometimes hinder the industrial implementation of many solutions. In fact, the introduction of waste as substitute for raw materials shall consider four main fundamental aspects (Zanelli *et al.*, 2021).

First, the technological behavior of the waste addition, that is the effect of the substitution on each specific step of the production process. As an example, the introduction of a waste can theoretically imply low to zero effects during the firing stage, affording a good quality ceramic product, but show a negative impact on rheology of suspensions or during the milling phase.

Secondly, the technical performance of a waste, which is the effect of the addition on the quality of final products, shall be also considered. Actually, even if there are no negative consequences during the manufacturing process and even if no aesthetic effects are visible on ceramic tiles, the addition of a component can hide a detrimental effect on, for example, the mechanical resistance of pieces, preventing in this manner a successful recycling.

The third aspect to pay attention on, is the environmental impact of the waste addition. This is a sensitive matter to which scientific production on recycling often do not pay enough attention. In fact, the strict regulations acting in the ceramic sector, especially in Italy, exhibit strict limits in terms of atmospheric emissions and waste disposal (2009/607/EC, 2009; Directive (EU) 2018/851 of the European Parliament and of the Council; *Gazzetta Ufficiale*). Thus, the adoption of mineral tailings or ashes deriving from thermal processes can induce collateral problems in terms of diffusion of heavy metals from air emissions or from leachates. Indeed, the inertization of hazardous compounds is an imperative precondition for waste recycling (Zacco *et al.*, 2014).

Finally, it is fundamental considering the economic sustainability of any recycling strategy. Often, in fact, natural occurring raw materials are simply the most economical choice. In addition, it can happen that the costs related to transportation or the additional costs due to pre-treatment of wastes preclude any otherwise competitive recycling option. However, it should be pointed out as the increasing strict character of environmental regulations concerning environmental protection will increasingly raise in the future the costs related to the exploitation of natural resources, levelling at the same time the cost discrepancy with nowadays expensive alternative materials (Porter and van der Linde, 1995). It is here suggested as to the economic sustainability of a raw materials shall be preferred all those aspects accounting for the overall sustainability of such materials, specifically the environmental and social aspects, in addition to economic ones. Conservation of delicate natural environments and reduction in waste generation are, in fact, among the objectives of sustainable development. Similarly, business with countries violating human rights or commercial trade of materials and products associated with the exploitation of human resources is hoped to be progressively restrained and severely sanctioned in the future. Unquestionably, the only pursue of economic profit is not contemplated in the funding values of a sustainable society (Feola, 2020). For these reasons, several recycling options that have not been implanted in the past because of the lack of economic advantages, can be probably available in the future.

In order to be recycled inside the production process of porcelain stoneware tiles, a waste shall be very similar to one of the main ingredients of the ceramic batches. That is, a new material shall provide plasticity or act as flux or as filler. In addition, a waste can also provide the function of main adopted additives, acting as dispersant, deflocculant or bactericidal. However, there are few examples in scientific literature and this case will not be treated here (Celik, 2014).

The majority of the wastes adopted by the ceramic industry act as a flux. This is principally due to the difficulty to replicate the plastic properties of clays or to emulate the refractory role played by quartz. In fact, when a material is recycled inside porcelain stoneware formulations to perform the role of filler, is usually by virtue of the high percentage of silica which is consisted of.

In the following sections, the main recycling options in the production process of porcelain stoneware tiles will be presented and commented, with a focus on the environmental impact and the technological behavior of new material additions.

2.2.1. Ceramic wastes

The large production volumes of ceramic tile factories have led, over the years, to the implementation of a vast number of internal waste recycling techniques that have made this industry a virtually zero-waste reality. In fact, almost the entirety of residues produces inside ceramic factories can be reutilized and reinserted inside production processes after zero to low loss of material. This is demonstrated by the deep and vast expertise of the Italian ceramic tile sector in the *Sassuolo* district (Busani, Palmonari and Timellini, 1995; Palmonari and Timellini, 2000; Resca *et al.*, 2021). However, as it is often the case for industrial realities, the scientific production on ceramic waste recycling does not reflect the actual situation and recycling solution as better kept under confidentiality.

During the production process of porcelain stoneware tiles, as described in **section 1.3**, wastes are generated as a results of purification process of water, the occurrence of flaws in products, yielding a various amount of both crude and fired tiles, the mechanical precipitation of solid particles inside air purification plants, tile polishing and cutting and collection of exhausted lime from kiln scrubbers.

Ceramic sludges arise after purification processes of water, which is used for the washing of most dusty environments, as spray-dryers allocation and decoration units, for tiles surface treatments and for glaze preparation. Correspondingly, ceramic sludges must be divided according to the content of fired or crude material. In fact, sludges containing crude powder can be easily reinserted inside ceramic bodies formulations with no compositional constraints. The only restrictions are related to the possible negative effects on rheology of slips as a consequence of the presence of impurities. Sludges containing fired material, on the other hand, are normally added to the milling phase in lower amounts with the function of filler, because of their refractory nature and high hardness. In this case, it must be taken into account the presence of impurities of SiC, used as abrasive, or magnesium oxychloride, employed as binder, as a consequence of the detriment of cutting and smoothing tools (Zanelli *et al.*, 2021). In addition, it was demonstrated as the direct use of water containing up to 5% on weight of ceramic sludges during the wet-milling of raw materials is possible (Andreola *et al.*, 2006).

The same considerations made for sludges containing crude materials are confirmed for crude tiles scrap. This waste consists mainly of broken crude tiles and derives, also, as a result collected dust from scrubbers and as residues of sieving devices. Because of the crystalline structures of raw materials have not yet been altered by the high temperatures of the firing stage, these scraps can easily be reinserted inside mills with virtually no constraints, having the same composition of the ceramic body. Even if the praxis is common among manufacturers, there are few examples in scientific literature (E. Rambaldi *et al.*, 2018).

On the other hand, fired scraps manifest a more refractory behavior and must be treated accordingly. These wastes come from the discarded flawed tiles after firing, or from unsold lots of tiles, usually stored in outside warehouses within ceramic factories.

Because of the sintering process results in the alteration of the crystalline phases of the raw materials and in a high hardness of the ceramic body, fired scraps require an additional milling for being recycled. The mechanical comminution can be promoted to various granulometries, according to the different action the waste shall perform. Higher granulometries are normally the choice for the use as filler while lower ones are accorded if a fluxing action is expected.

The exhausted lime ($Ca(OH)_2$) is collected as a result of the chemical depuration of air emissions stemming from the firing stage. It is a fine powder of calcium hydroxide and a mixture of other chemical species (CaF_2, $CaSO_4$ and other calcium related salts). resulting from the reactions with the most reactive compounds contained in the exhausted fumes. However, if in this case there are various examples inside the scientific literature of recycling in ceramic production, the utilization of such waste is basically never implemented because negative environmental impact. In fact, fluorine is released during firing starting from 800 °C and, beyond 1000 °C, the techniques to trap fluorine ions inside the reticule of crystalline phases becomes vane (Monfort *et al.*, 2008). Furthermore, exhausted lime is considered hazardous waste by Italian legislation and must be treated accordingly (*Gazzetta Ufficiale*). Therefore, exhausted lime is the only waste of the production process of porcelain stoneware tiles which is actually not recycled. However, the far higher quantity of all above mentioned wastes produced along the manufacture, grants a total recycling percentage of solid waste around 100% and, in certain cases, above this value (Timellini *et al.*, 2008). In fact, as previously mentioned, this industrial sector is able to welcome different materials as a source of recycling, as it will be shown in the following sections.

2.2.2. *Demolition waste*

The recycling of construction demolition wastes in the industrial manufacturing of porcelain stoneware tiles can be theoretically implemented making the same considerations made for fired scrap. In fact, these kinds of wastes are usually a mixture of bricks, stone, concrete and mortars which are, basically, very similar in composition to ceramic bodies and can thus be used as fillers inside formulations for porcelain stoneware. However, there are different technical barriers to the implementation of such solution. In the first place, the great variability in composition due to practical difficulties during collection of wastes, prevents the use of a single specific residue as a substitute for natural raw materials (Rodrigues *et al.*, 2013). Secondly, the possible presence of heavy metals as Cr, Mo, Pb, Fe, Se or of chemical species of Cl and S prevents most of the recycling options for demolition wastes (Delay *et al.*, 2007; Butera, Christensen and Astrup, 2014).

In scientific literature, there are some examples of the recycling of asbestos fibers inside ceramic products as, for example, in glass-ceramic frits destined to the manufacturing of porcelain stoneware slabs (Ligabue *et al.*, 2020). However, the complex pre-treatment required to make such residue harmless preclude an easy recycling.

In conclusion, it can be asserted as the recycling of demolition wastes is poorly conducted in the ceramic sector, mainly because of economic reasons related to selective collection of wastes.

On the other way around, the recycling of ceramic waste in the construction sector is far more implemented. In fact, fired ceramic residues, obtained from flawed tiles and from unsold lots, are efficiently used as refractory aggregates in concrete production, as demonstrated by the reach scientific literature (Medina, Sánchez de Rojas and Frías, 2013; Ray *et al.*, 2021).

2.2.3. *Glass*

Among the most used waste materials in ceramic manufacturing, there is certainly glass. It is mainly an amorphous material with no to little presence of crystalline components. By virtue of the high abundance of material, its high fusibility and the low composition variability of glass sources, it has been vastly adopted as a substitute for feldspars in composition of different types of ceramic tiles, from vitrified to porous bodies. The presence of important percentages of sodium oxides (Na_2O) and calcium oxides (CaO), and poor amounts of alumina inside glass composition, are able to reduce the firing temperatures of ceramic tiles, allowing at the same time a reduction in natural raw material consumption and in CO_2 emissions, related to a lower gas expenditure (Raimondo *et al.*, 2007; Silva *et al.*, 2017; Zanelli *et al.*, 2021). In addition, the scarce occurrence of titanium and iron oxides inside glass prevents any darkening effect on ceramic bodies, as it is often the case in the adoption of waste materials in ceramic manufacture.

The two most exploited glass sources come from flat and container glass, known as soda-lime-silica (SLS) glass, and from a vast variety of waste electrical and electronic equipment (WEEE), possessing different distinctive chemical compositions depending on the nature of parent equipment (TV-screen, lamp bulb, cathode ray tube, etc.).

There scientific literature on glass recycling in porcelain stoneware tiles manufacturing is particularly reach, with some important examples on semi-industrial scale or full industrial applications (Matteucci *et al.*, 2002; Pontikes *et al.*, 2005; Rambaldi, *et al.*, 2018; Skerratt, 2001; Tucci *et al.*, 2004).

However, there are some technical barriers for a full-profit recycling opportunity of glass. In particular, glass cullet require a previous grinding treatment in order to be reintroduced inside the production process of tiles. In addition, even if the chemical composition of glass itself is particularly clean and constant among glass sources, often this material is employed in combination with other materials which makes separation processes quite challenging. For example, flat glass is often associated with a polymeric sheet for safety reasons in its application in cars windshields. Further, glass is used as a physic protection of silicon wafers in solar panel modules in a sandwich-like structure with poly-(ethylene-vinyl acetate) sheets. Again, in lamp bulbs, glass and metal components are strictly combined. This makes separation processes or not perfectly effective or particularly expensive, with the corresponding collateral consequences of the presence of impurities negatively affecting the rheology and firing stages of ceramic pieces, or simply of making the recycling of glass not economically feasible. In addition, some glass sources can carry relevant quantities of hazardous components, as it is the case of cathode ray tube glasses, incorporating high percentages of lead oxide (PbO) as a chemical shield for electron beams. Other heavy metals contained in recycled glass sources are As and Sb, Hg, and Ba (Rey-Raap and Gallardo, 2012; Savvilotidou, Hahladakis and Gidarakos, 2014; Zanelli *et al.*, 2021). However, it shall be highlighted as in the case of glass the intertization of the hazardous species is particularly effective and the above mentioned glass sources have been efficiently employed in the production of porcelain stoneware tiles with no negative effect on the quality of leachates (Raimondo *et al.*, 2007; Andreola *et al.*, 2008; E Rambaldi *et al.*, 2018).

The main effect of glass inside formulations for porcelain stoneware is to enhance fusibility of the ceramic body, often resulting in a reduction of the firing temperatures. The effects on other properties of tiles, as the mechanical strength, the resistance to scratch abrasion, the chemical and frost-thaw resistance, are of various magnitude, depending on both the amount of the glass additions and on the chemical nature of it. In fact, recycling of glass stretch from 2-5% of addition up to higher percentages, up to 40% in porcelain stoneware formulations, with all different cases in between (Tucci, Rambaldi and Esposito, 2006; Kim, Kim and Hwang, 2016).

Finally, ceramic glazes and engobes are two further recycling options for glass scrap. In this case, glass is used in the synthesis of frits as a silica source and melting agent or as their substitute in combination with clays in glazes and engobes formulations (Andreola *et al.*, 2007; Dal Bó, Bernardin and Hotza, 2014).

2.2.4. *Mining residues*

These wastes include residues from quarrying operations, from purification mechanism of natural rocks, from mineral beneficiation, mineral tailings and sludges from stone cutting. Such materials are normally stored near extraction sites in big ponds in outside environments, as illustrated in **Figure 2-2**. The precarious storing conditions, together with the often-scarce maintenance and the exposition to atmospheric events, can pose a serious risk of releasing huge quantities of hazardous wastes. This situation represents a serious environmental threat which can sometimes tragically evolve into environmental disasters, as the *Brumadinho* dam disaster, where a tailing dams suffered a destructive failure, resulting in the release of 12 million cubic meters of tailings into land (Vergilio *et al.*, 2020).

Figure 2-2. Tailing ponds containing mining residues near an extraction site in Utah, U.S.A, from (Canadian Mining Journal).

Although the scientific production on the recycling of mining residues in the ceramic sector is particularly rich, the number of cases related to porcelain stoneware tiles are few. The majority of case-studies focus on the manufacturing of red firing wall tiles and on porous bodies as well on artificial stones (Zanelli *et al.*, 2021).

Examples of application of mining residues in porcelain stoneware tiles are scarce principally because of the high sensitivity of this type of material towards impurities of iron or other metallic species, present inside these waste as a consequence of deterioration events on cutting and sawing tools or because natural occurring in parent rocks.

The role performed by mining residues is as fillers or as fluxing agents, depending on the quartz-feldspar ratio. As an example, residues from borate processing are recycled in formulations of porcelain stoneware tiles as substitute of feldspars by virtue of their fluxing character, in concentration up to 20% (Korç *et al.*, 2018). However, most of cases consider far lower percentage of addition, ranging from 3 to 10% (Ediz and Yurdakul, 2009; Zanelli *et al.*, 2019; Karadagli and Cicek, 2020). An important case of industrial application of mining residues, is the exploitation of granite waste as flux inside formulation for porcelain stoneware (Carbonchi *et al.*, 2013). Other interesting works maintain the investigation at laboratory level or, even, at the level of formulation design. Among these, are worth citing the utilization of agate rejects inside porcelain stoneware batches as a substitute for quartz and the use of mineral tailings containing iron for the development of red and brown porcelains (Chen *et al.*, 2013; Fontes *et al.*, 2019).

2.2.5. Incinerated ashes

It is here referred to incinerated ashes as the products of incineration processes of various types of organic matter, generally for thermal valorization purposes. The result is a mixture of ashes characterized by various granulometries and chemical compositions. The two principal residues are bottom ashes, coarse and clinker like particles of a mainly inorganic nature and remaining traces of combustible, and fly ashes, which are finer particles transported by flue gasses, composed mostly by silica and aluminum oxide, together with a more or less content of concentrated heavy metals (US EPA, 2014). Examples of bottom and fly ashes are reported in **Figure 2-3**.

Figure 2-3. Examples of combustion residues of energy valorization thermal processes: bottom ashes (left) and fly ashes (right), from (*Fly Ash | Buildex; Incinerator Bottom Ash – Preparation, Testing and Monitoring*).

However, the exact composition of these ashes is strongly related to the fuel adopted for combustion and to the nature of parent materials. These are hazardous wastes produced at the rate of over 50 million tons per year, which are generally stored in ponds or dumped in landfill sites and, thus, recycling strategies to reuse such residues are critically compelled (Kim and Prezzi, 2008).

There are few examples of recycling of incinerated ashes in the manufacturing process of porcelain stoneware tiles and in most of cases investigation is maintained at laboratory level (Zanelli *et al.*, 2021). In fact, this special class of wastes, by virtue of the incredibly vast chemical composition, is more easily committed to recycling option in the construction sector, especially in concrete production, as road sub-base or in the synthesis of geopolymer materials (Ahmaruzzaman, 2010; Singh and Siddique, 2013; Mehta and Siddique, 2016).

Notwithstanding such scarcity, there are still some examples of recycling in porcelain stoneware formulations. For examples, coal bottom and fly ashes have both been tested as partial substitute of felspars and quartz in the production of porcelain stoneware tiles (Dana, Dey and Das, 2005; Prasartseree *et al.*, 2018). Normally, the high content of Fe_2O_3 in these types of ashes induce dark tones to ceramic bodies.

In addition, municipal solid waste incinerator (MSWI) ashes were used after de-ironization process as feldspar substitute up to 10% percentages in formulation of porcelain stoneware, without negatively affecting quality of leachates (Rambaldi *et al.*, 2010). Indeed, the composition of these ashes, rich in alkaline and alkaline earth oxides, grant good possibilities of recycling as flux agent but high consideration shall be directed in controlling the inertization of heavy metal species and in managing the release of chlorine and sulfur compounds at the air emissions during firing of ceramic pieces.

Other ashes that have been investigated as possible substitute raw materials for porcelain stoneware are those arising from thermal valorization of biomass. Interesting examples are the use of ashes from incineration of sugarcane bagasse, fish bones or rice straw, introduced in the production of porcelain stoneware tiles and the use of rice husk ashes in the synthesis of a ceramic glaze (Bondioli *et al.*, 2010; Naga *et al.*, 2014; Guzmán A *et al.*, 2015; Schettino and Holanda, 2015). However, the same considerations done for MSWI ashes are valid in this case and the environmental impact arising from the implementation of such recycling strategies shall be carefully considered.

2.2.6. *Waste from metal industry*

This class of waste materials includes slags deriving from both ferrous and non-ferrous metallurgy, and spent foundry sands and galvanic sludges, two residues coming correspondingly from metal casting and metal coating processes. Chemical compositions depends on the parent process and nature of metal involved, but similar characteristics can be highlighted for each specific waste. For example, furnace slags are usually reach in calcium oxide (CaO) and magnesium oxide (MgO) and poor in silica, with iron content strongly depending on the type of furnace. On the other hand, foundry sands are rich in silica and iron oxide (Fe_2O_3) while galvanic sludges can present heavy metals as Cr, V, Zn and Ni in considerable amounts. However, in all mentioned wastes, special attention shall be directed to the immobilization of hazardous metallic species inside the glassy matrix, preventing any possibility of leaching of toxic ions. Furthermore, even if in most of cases the addition of the waste is carried out with any pre-treatment on a laboratory scale, the presence of metal impurities and the high hardness of these materials would require preliminary grinding and other purification treatments before any chance of introduction in an industrial manufacturing process.

Usually, such wastes are employed as substitute for feldspars by virtue of their fluxing action, but there are few examples of the use of such wastes inside porcelain stoneware bodies (Dana, Dey and Das, 2005; Das *et al.*, 2013; Siddiqui *et al.*, 2014; Zhao *et al.*, 2015; Pal *et al.*, 2016; Zanelli *et al.*, 2021). In addition, because of the high amount of iron, the recycling is restricted to dark firing ceramics.

Conversely, the recycling of waste from metal industry is far more practiced in the synthesis of glazes and pigments for the ceramic industry. In this case, the high occurrence of chromophores and darkening oxides inside residues can be profited for the obtainment of pigments characterized by great coloring properties (Hajjaji *et al.*, 2012; Carneiro *et al.*, 2018; Vilarinho *et al.*, 2021). In this case, possible drawbacks are related to poor color stability and variability in the chemical composition of wastes.

2.2.7. *Other waste materials*

In scientific literature, it can be found a series of further recycling options in ceramic manufacture for other materials whose exhaustive description has been deliberately omitted. Among other waste sources there are water sewage sludges, glasses from waste melting, residues from paper production, as paper mill and cellulose sludges, oily sludges from oil refining and residues from industrial production of chemicals (Zanelli *et al.*, 2021). In all cases, investigation of recycling opportunities was restricted to laboratory scale. Furthermore, all cited wastes, besides concealing common drawbacks as non-negligible content of heavy metals, would require preliminary treatments as, for example, de-watering, milling, de-ironization or calcination, preventing any access to possible economic recycling prospects.

Nonetheless, it should be reminded here that some of the above-mentioned technological constraints can be overcome in first place through encouraging scientific research on waste recycling and by increasing investments in this field. On the other hand, the relaxation of severe market requirements, especially concerning aesthetical appearance and fascination for light-firing ceramic bodies, can play an important role in making some of the illustrated waste sources appealing for recycling in porcelain stoneware tiles manufacturing.

2.3. ISO 17889-1:2021 Ceramic tiling systems – Sustainability for ceramic tiles and installation materials

Published in 2021, the standard ISO 17889-1 "Ceramic tiling systems – Sustainability for ceramic tiles and installation materials-Part 1: Specifications and vocabulary for ceramic tiles" was devised upon proposal of the Italian committee within the ISO commission (ISO 17889:2021). The standard defines a rating system for the sustainability of ceramic tiles all over the entire life cycle of the products, covering the design, production, installation and utilization phases.

It has been devised a multi-rating system adopting 38 criteria divided according to the three pillars of sustainability: the social, environmental and economic aspects. In order to comply with the standard, a ceramic tile product shall match 15 mandatory requirements and obtain a minimum score of 117.5 on a maximum of 130 as a sum for the 23 multi-rating criteria.

It is highlighted as ISO 17889-1 is a product standard and whenever there is a wish to extend the application of the standard to the whole internal production of a company, reference should be made to the worst-case scenario found among the product portfolio.

In particular, the mandatory requirements refer to:

- Raw materials register: the manufacturer shall possess a list of all raw materials used in the final product, including the corresponding safety data sheet for each material.
- Contract of purchase for raw materials and environmental services: it is required a written statement concerning the environmental policy issued by each direct supplier of raw materials and from suppliers of outsourced manufacturing and packaging services.

- Fuel adopted: any manufacturing unit producing the final product shall utilize no other fuel than natural gas, liquid petroleum gas, methane from biomasses or bio combustibles.

- Reuse/recycling or separate collection of auxiliary materials: the manufacturing plant shall display mechanisms to internally reuse or externally recycle or, again, to carry out a separate collection of plastics, metals, worn packaging, exhausted oil, etc.

- Ecological installation: the manufacturer shall provide instructions to the installer concerning the proper execution of installation operations with particular concerns to environmental aspects and the responsible management of packaging materials during this phase.

- Ecological flooring maintenance: the manufacturer shall provide instructions to the user concerning the proper maintenance of the product, specifying the use of the least hazardous and most environmentally friendly cleaning agents.

- Ecological flooring disassembling: the manufacturer shall provide information indicating the proper separation procedure and management of waste materials coming from the dismantling process of tiles.

- Compliance to product's standard and to manufacturer's declarations: the manufacturer shall demonstrate that the product is complying with the standard ISO 13006:2018 and communicate results, if asked for.

- Information to workers on the risks of exposure to chemical and physical agents: the manufacturer shall inform workers and raise awareness within workplaces on the possible hazards related to the use of chemical and physical agents.

- Dust removal and filtration systems within the working units: it shall be demonstrated that the dust removal and filtration systems are in good working condition, as required by the specification of the equipment, especially in the following working units: receiving and milling of raw materials, atomization, pressing, preparation and application of glazes.

- Contract of purchase for raw materials and health and safety services: it is required a written statement concerning the health and safety policies issued by each direct supplier of raw materials and from suppliers of outsourced manufacturing and packaging services.

- Information to the dealer and the installer: the manufacturer shall provide information regarding the proper and safe handling of the product in relation to its weight and size and dispense guidelines for a safe cutting procedure of tiles.

- Safety data sheets of materials: the manufacturer shall provide availably of the safety data sheets of tiles to the dealer and the installer.

- Information to the user on proper utilization of the product: the manufacturer shall inform the user on the proper use and maintenance of the ceramic flooring.

- Contract of purchase for raw materials and outsourced services in accordance with the labor law: it is required a written statement by each direct supplier of raw materials and from suppliers of outsourced services concerning the compliance to national labor laws and regulations.

On the other hand, multi-rating criteria are subdivided in three categories, each one contributing with a different weight on total rating:

V_1: complying/not complying (weight: 1)

V_2: management requirements (weight: 3)

V_3: performance indicators (weight: 6)

The rating systems specifies a variable score of 100, 110, 120 and 130%. The final score, ranging from 100 and 130% is calculated as a weighted average of the scores obtained for each category of criteria.

As previously mentioned, the present standard defines as sustainable products those tiles complying with all the mandatory requirements and obtaining a minimum score of 117.5%.

2.4. Environmental labels

The series of EN ISO standards 14020 declares all general principles for the development and usage of environmental labels, according to three types of voluntary declarations (ISO 14020:2000). Those belonging to type I follow the guidelines stated in the norm EN ISO 14024:2018 and require certification by an independent body (ISO 14024:2018). These certifications are developed on a scientific basis and require compliance with several specific limits regarding, for example, the resource consumption and the use of energy. Amongst these labels there is the EU Ecolabel, which will be described in detail in the next. Certifications of type II, according to the norm EN ISO 14021:2016, comprehend a whole set of environmental claims made by manufacturers, importers or distributors of products, without the intervention of an independent certification body (ISO 14021:2016). Under this type of environmental declarations fall all the auto-declared symbols and claims regarding various issues as, for example, the reduction in natural resources or energy consumptions, the smart design, the compostability or biodegradability or the percentage of recycled material in the manufacturing of a specific product, as represented by the Möbius’ cycle symbol in **Figure 2-4**.

Figure 2-4. Representation of the universal recycling symbol under the form of a Möbius loop or cycle.

The EPD (Environmental Product Declaration), described in **section 2.4.2**, is a type III declaration. According to the guidelines stated in the norm EN ISO 14025:2010, these declarations make claims based on established parameters and contain a quantification of the environmental impacts associated with the product's life cycle calculated through an LCA system. Claims and environmental performances are in this case independently audited and presented in a clear and comparable form. In the next sections the most recognized environmental labels are described, with a particular focus on the EU Ecolabel and on the EPD related to ceramic tiles.

2.4.1. EU Ecolabel – Hard coverings

The EU Ecolabel is one of the most recognized and relevant label for environmental excellence. It was officially established in 1992 by the European Union and, since then, it certifies the optimal environmental performance of products and services at global levels. The EU Ecolabel sets high environmental standards regarding the consumption of natural resources, atmospheric emissions, recycling rates and safety aspects on the whole life cycle of products, from the raw materials extraction through manufacturing and use to disposal. Products and services must both meet all mandatory requirements and achieve a minimum overall score to qualify for the EU Ecolabel. Furthermore, the label also encourages sustainable design practices that ensure less material consumption as well as longer product lifetimes and easier recycling.

This kind of environmental labels can help consumers to choose for more sustainable products and direct the market demand toward more conscious consumption practices, actively contributing to the sustainable development of technology and society.

The EU Ecolabel criteria for ceramic floorings are set by the recently amended version of the EU Ecolabel – Hard coverings through the Commission Decision (EU) 2021/476 of 16 March 2021 (Commission Decision (EU) 2021/476). These criteria will be in force until the 31st of December 2028 when, after another technical assessment of the environmental performance of the ceramic tile sector, new standards will be established.

The specific criteria related to materials consumption and involved technology for ceramic and bricks concern the fuel consumption of the drying and firing stages, the total CO_2 emissions, the water consumption, the atmospheric emissions of particulate matter, hydrofluoric acid, nitrogen and sulfur oxides, the management of waste water and solid waste and the use of inks and glazes. In particular, for the purpose of this thesis, it is reported in **Table 2-1** the list of the mandatory requirements and excellence thresholds concerning the atmospheric emissions of most characteristic pollutants and the reutilization of waste.

Table 2-1. EU Ecolabel's mandatory requirements and excellence performance thresholds for the atmospheric emissions of pollutants and waste reutilization, as state by the Commission Decision (EU) 2021/476.

Parameter	**Process**	**Mandatory requirement**	**Excellence threshold**
		(mg/kg)	
Dust	Spray-drying	90	n.a.
	Firing	50	10
HF	Firing	20	6
NO_x (as NO_2)	Firing	250	170
SO_x (as SO_2)	Firing	1 300	750
Parameter	**Process**	**(%)**	
Re-use of waste*	Whole manufacturing process	50	50-100

(*) In this case "waste" indicates unfired and fired tiles scrap, fired ceramic powder from surface treatment operation, powder waste from filtering devices and ceramic
n.a.: not applicable

The applicant must provide data for the production site in mg/Nm^3 as a daily average value. The conversion from mg/Nm^3 to mg/kg of ceramic product is then done by multiplying the former value by the specific volume of gaseous effluent (Nm^3/kg). For the mandatory requirements and excellence limits regarding the other criteria, refer to the above-mentioned directive.

2.4.2. EPD – Environmental Product Declaration

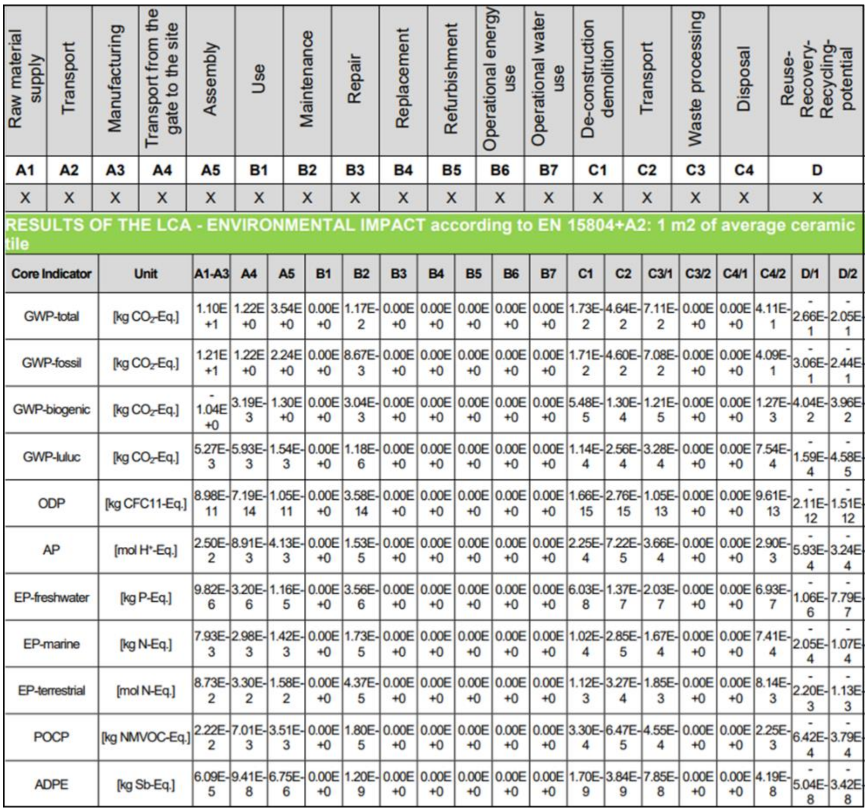
The Environmental Product Declaration (EPD) is another useful tool designed to convey the environmental performance of products and to facilitate the environmental communication between manufacturers and consumers on the market stage (**Figure 2-5**).

Figure 2-5. Environmental Product Declaration label.

Conceived according to EU environmental policies and adopted on a voluntary basis, the EPD is based on the application of the LCA (Life Cycle Assessment) methodology and address the overall environmental impact of a products on its overall life cycle. The LCA is implemented following the guidelines of the standard EN ISO 14025 (ISO 14025:2006).

Results are then presented in summary by using specific environmental indicators per declared unit of product (*e.g.* liter, kg or ton). Among the indicators adopted, it is here worth mentioning the GWP (global warming potential), the AP (acidification potential), the ODP (ozone depletion potential), the ADP (abiotic depletion potential), the RM (use of recycled material) and the PERT (total use of renewable primary energy resources). In this manner, the information regarding the sustainability of products can be objective and comparable, making the industrial manufacturing processes more transparent and enabling distributors and consumers to make more informed choices when purchasing goods.

Various Italian ceramic companies have published environmental product declarations regarding their top quality products, demonstrating a remarkable commitment in accessing transparent information on sustainability issues (*EPD Italy*). In addition, the association of the Italian ceramic tile manufacturers *Confindustria Ceramica* has published the EPD of the ceramic tile sector. The last updated version addressed the main characteristics of ceramic tiles, the production process, the constituents, the conditions of installation and disposal and health issues related to the use. Then, the results of the life cycle assessment are presented through a series of 25 environmental indicators, listed starting from the raw material supply to the reuse and recycling potential after disposal. In **Figure 2-6** the performance indicators concerning the environmental impact of one square meter of average ceramic tile (19.9 kg/m^2) are illustrated.



Raw material supply	Transport	Manufacturing	Transport from the gate to the site	Assembly	Use	Maintenance	Repair	Replacement	Refurbishment	Operational energy use	Operational water use	De-construction demolition	Transport	Waste processing	Disposal	Reuse-Recovery-Recycling-potential
A1	**A2**	**A3**	**A4**	**A5**	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**C1**	**C2**	**C3**	**C4**	**D**
X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

RESULTS OF THE LCA - ENVIRONMENTAL IMPACT according to EN 15804+A2: 1 m2 of average ceramic tile

Core Indicator	Unit	A1-A3	A4	A5	B1	B2	B3	B4	B5	B6	B7	C1	C2	C3/1	C3/2	C4/1	C4/2	D/1	D/2
GWP-total	[kg CO_2-Eq.]	1.10E+1	1.22E+0	3.54E+0	0.00E+0	1.17E-2	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	1.73E-2	4.64E-2	7.11E-2	0.00E+0	0.00E+0	4.11E-1	-2.66E-1	-2.05E-1
GWP-fossil	[kg CO_2-Eq.]	1.21E+1	1.22E+0	2.24E+0	0.00E+0	8.67E-3	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	1.71E-2	4.60E-2	7.08E-2	0.00E+0	0.00E+0	4.09E-1	-3.06E-1	-2.44E-1
GWP-biogenic	[kg CO_2-Eq.]	-1.04E+0	3.19E-3	1.30E+0	0.00E+0	3.04E-3	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	5.48E-5	1.30E-4	1.21E-5	0.00E+0	0.00E+0	1.27E-3	4.04E-2	3.96E-2
GWP-luluc	[kg CO_2-Eq.]	5.27E-3	5.93E-3	1.54E-3	0.00E+0	1.18E-6	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	1.14E-4	2.56E-4	3.28E-4	0.00E+0	0.00E+0	7.54E-4	-1.59E-4	-4.58E-5
ODP	[kg CFC11-Eq.]	8.98E-11	7.19E-14	1.05E-11	0.00E+0	3.58E-14	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	1.66E-15	2.76E-15	1.05E-13	0.00E+0	0.00E+0	9.61E-13	-2.11E-12	-1.51E-12
AP	[mol H^+-Eq.]	2.50E-2	8.91E-3	4.13E-3	0.00E+0	1.53E-5	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	2.25E-4	7.22E-5	3.66E-4	0.00E+0	0.00E+0	2.90E-3	-5.93E-4	-3.24E-4
EP-freshwater	[kg P-Eq.]	9.82E-6	3.20E-6	1.16E-5	0.00E+0	3.56E-6	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	6.03E-8	1.37E-7	2.03E-7	0.00E+0	0.00E+0	6.93E-7	-1.06E-6	-7.79E-7
EP-marine	[kg N-Eq.]	7.93E-3	2.98E-3	1.42E-3	0.00E+0	1.73E-5	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	1.02E-4	2.85E-5	1.67E-4	0.00E+0	0.00E+0	7.41E-4	-2.05E-4	-1.07E-4
EP-terrestrial	[mol N-Eq.]	8.73E-2	3.30E-2	1.58E-2	0.00E+0	4.37E-5	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	1.12E-3	3.27E-4	1.85E-3	0.00E+0	0.00E+0	8.14E-3	-2.20E-3	-1.13E-3
POCP	[kg NMVOC-Eq.]	2.22E-2	7.01E-3	3.51E-3	0.00E+0	1.80E-5	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	3.30E-4	6.47E-5	4.55E-4	0.00E+0	0.00E+0	2.25E-3	-6.42E-4	-3.79E-4
ADPE	[kg Sb-Eq.]	6.09E-5	9.41E-8	6.75E-6	0.00E+0	1.20E-9	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	1.70E-9	3.84E-9	7.85E-8	0.00E+0	0.00E+0	4.19E-8	-5.04E-8	-3.42E-8

Figure 2-6. Results for the LCA concerning the environmental impact of 1 m^2 of ceramic tile (*EPD the environmental product declaration for Italian ceramic tiles - Confindustria Ceramica*).

The data reported in the figure refer to the last updated version of the sectorial EPD, issued on 4th January 2023. Sectorial environmental declarations represent certainly a less faithful description of the actual impact of a certain product with respect to the series of environmental indicators of a common LCA. In fact, the environmental performance related to a specific tile, especially due to differences in thickness, amount of glaze and surface treatment, can vary considerably (Ros-Dosdá *et al.*, 2018). At the same time, however, these declarations can be a useful tool for discriminating between the environmental impacts of different classes of products used for the same purpose, such as, in the case of tiles, floor covering materials (Ros-Dosdá *et al.*, 2019).

2.4.3. *Other voluntary sustainability and quality labels*

Besides the environmental product declaration, the EU Ecolabel and the ISO standard 17889-1, there are other voluntary declarations that ceramic companies can exhibit in order to demonstrate their commitment to sustainability issues. The following ones, however, are not product certifications, but rather building-related certifications, to which the choice for more sustainable flooring solutions can contribute accessing.

One among the most important and internationally recognized green building certification is the LEED certification system (Leadership in Energy and

Environmental Design, (*USGBC | U.S. Green Building Council*). It is one of the most recognized and used green rating systems aimed for both commercial and residential buildings. The LEED certification is implemented through the compliance process to various green building design standards by using a point system concerning five main areas regarding sustainable sites, water efficiency, energy and atmosphere, materials and resources and indoor environmental quality. Building and homes, according to the obtained score, up to a maximum of 110 points, are then awarded with one of the four levels of LEED certification (**Figure 2-7**): the basic LEED (between 40 and 49 points) or the silver (between 50 and 59 points), gold (between 60 and 70 points) or platinum certifications (beyond 80 points).

Figure 2-7. The four levels of LEED's green building certification.

Finally, it is here presented the BREEAM as a last green building certification to which ceramic tiles can contribute. The BREEAM (Building Research Establishment Environmental Assessment Method) is a voluntary certification system aimed at the certification and classification of the environmental sustainability of buildings (**Figure 2-8**)(*BREEAM | BRE Group*, 2022).

Figure 2-8. The BREEAM's green building certification.

In this case the rating process is carried out by a properly trained professional auditor belonging to the Building Research Establishment of London, who report the score of BREEAM credits according to the following categories: management, health and well-being, energy use, involved transport, water and materials use and consumption, production of waste, land use and environmental pollution.

2.5. Industrial emissions – European context

The environmental impact of industrial activities operating in the European Union is regulated by the Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008, known as Integrated Pollution Prevention Control (IPPC) Directive, and by Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010, also known as Industrial Emissions Directive (IED) (Directive 2008/1/EC, 2008; Directive 2010/75/EU, 2011).

In particular, the IED derives after a major review of existing policies on environmental pollution, including the IPPC directive, with which shares the integrated approach and the prevention aspect.

The main objectives of the environmental policy of the European Community are the prevention and reduction of pollution through the rational management of natural resources and according to the polluter pays principle. In addition, the integrated approach focuses on integrating preventive actions aimed at the reduction of environmental pollution in its entirety and not, conversely, on distinct approaches to contain emissions into air, water and soil. In fact, it is suggested that such a separate approach may facilitate the transfer of pollutants from one sector to another.

The IED grants the protection of human health and environment, in particular through better application of Best Available Techniques (BAT) and BAT-associated environmental performances at European level. Experts from Member States, industry representatives and environmental organizations are committed to a vast data collection process and exchange of information which eventually results in the publication of the BAT Reference Documents (BREFs). These documents are taken as reference for communicating operating permits to industrial entities. In addition, every three years, the European Commission is provided with representative data on emissions performance and actual existing limits, according to each industrial category.

According to the directive, operating permits to new industrial installations or alterations on existing plants shall be accorded exclusively after validation of local authorities and only if it is demonstrated that all prospects for pollution prevention have been considered. In this manner, it is possible to evaluate and take record of any possible source of pollution. Such operating permits are accorded upon issuing of legal documents known as Integrated Environmental Authorizations (IEAs), including all series of information characterizing the industrial installation and regarding the management of emissions and waste production. However, a fundamental aspect of the IED and IPPC Directive is related to the importance of local environments around industrial plants. The existing situation, such as the actual air quality and geographical location, should be taken under consideration when deriving emission limits, without the exclusive observation of the best available techniques. Member States will be then responsible for the interpretation of each specific environmental background. Thus, if an environmental quality standard requires more rigorous conditions than those articulated inside BREF documents, local authorities can include additional measures in the permit. On the other hand, if it is demonstrated that BAT performances cannot be realized because of the existence of economic constraints, then the accorded emission limits can result higher than the BAT associated emission levels (BAT-AEL) stated inside BREF documents. In fact, BAT-AEL does not define but only suggest emission limit values (ELVs). Conversely, the limits reported in the IED for certain pollutants and for specific sectors are legally binding.

Nonetheless, the most important character of these environmental regulations is represented by their transparency and liability to public participation. In fact, environmental reports from industrial installations, as well as operating permits and legal documents concerning authorizations and inspections from local authorities, are published online on public domain portals and are continuously updated.

Finally, it should be highlighted here as the IED does not interfere with the ETS directive, specifying limits for greenhouse gases only in particular cases.

2.6. Industrial emissions – Italian ceramic tile sector

In Italy, the above-mentioned European directives are implemented through the Italian decrees D. Lgs. of 4 March 2014, n° 46, D. M. of 29 January 2007 and D. Lgs. of 3 April 2006, n° 152 (*D. M. 29 Gennaio 2007; D. Lgs. 3 Aprile 2006, n. 152; D. Lgs. 4 Marzo 2014, n. 46*). In particular, the last decree states all guidelines for the environmental impact assessment of industrial installations and all requirements for the release of the Integrated Environmental Authorization, or *Autorizzazione Integrata Ambientale* (AIA), in Italian. The AIA covers the whole lifespan of the installation, considering not only working conditions, but also the disposal phase and transitory inactive periods.

In the case of ceramic tile factories, the AIA is considered a mandatory legal requirement only for those installations with a production capacity over 75 ton per day. However, the majority of ceramic tile factory easily outperform such production. All other entities are regulated through the *Autorizzazione Unica Ambientale* (AUA), which is another environmental authorization, sharing the main integrated approach of environmental protection with the AIA, but simplifying the authorization process and easing the bureaucracy. Both AIA and AUA documents are released by the local competent authority, which is, in each region of Italy, the regional bureau of ARPA

(*Agenzia Regionale per la Protezione Ambientale*), the environmental protection body of the Italian public administration. All AIA documents of ceramic tile manufacturing installations located in Emilia-Romagna are available online on the web portal of ARPAE, the environmental protection agency of Emilia-Romagna region (*Homepage - Autorizzazione Integrata Ambientale - Regione Emilia Romagna*). According to the IED, ceramic tile factories are assigned with the code 3.5, defining the "manufacture of ceramic products by firing", and belong to the mineral industry (activity code 3).

The best available techniques operating in the ceramic tile sector, as well as in other related sectors as the bricks and refractories manufacturing, are stated in the CER BREF, which is the BAT-Reference documents for the ceramic industry (*Ceramic Manufacturing Industry | Eippcb*). The current version of the CER BREF dates back to 2007 and a new version is actually under revision. All BREF documents are of public domain and are available online on the portal of the European Integrated Pollution Prevention Control Bureau (EIPPCB) (*Front Page | Eippcb*).

On the other hand, the above-mentioned decree D. M. of 29 January 2007 sets out the guidelines to be adopted in Italy for the identification and use of best available techniques for activities under IPPC category 3.5. In this case, the suggested threshold limits were obtained based on the current level of best available techniques in the Italian ceramic tile industry.

In **Table 2-2** are reported the BAT-AELs according to the BREF and the Italian decree D. M. of 29 January 2017, regarding the manufacturing of wall and floor tiles, which is the reference sector for porcelain stoneware tiles.

Table 2-2. BAT-AEL relating to air emissions and reuse of materials for the production process of porcelain stoneware tiles, as stated in the CER BREF document and by the Italian decree D. M. of 29 January 2017.

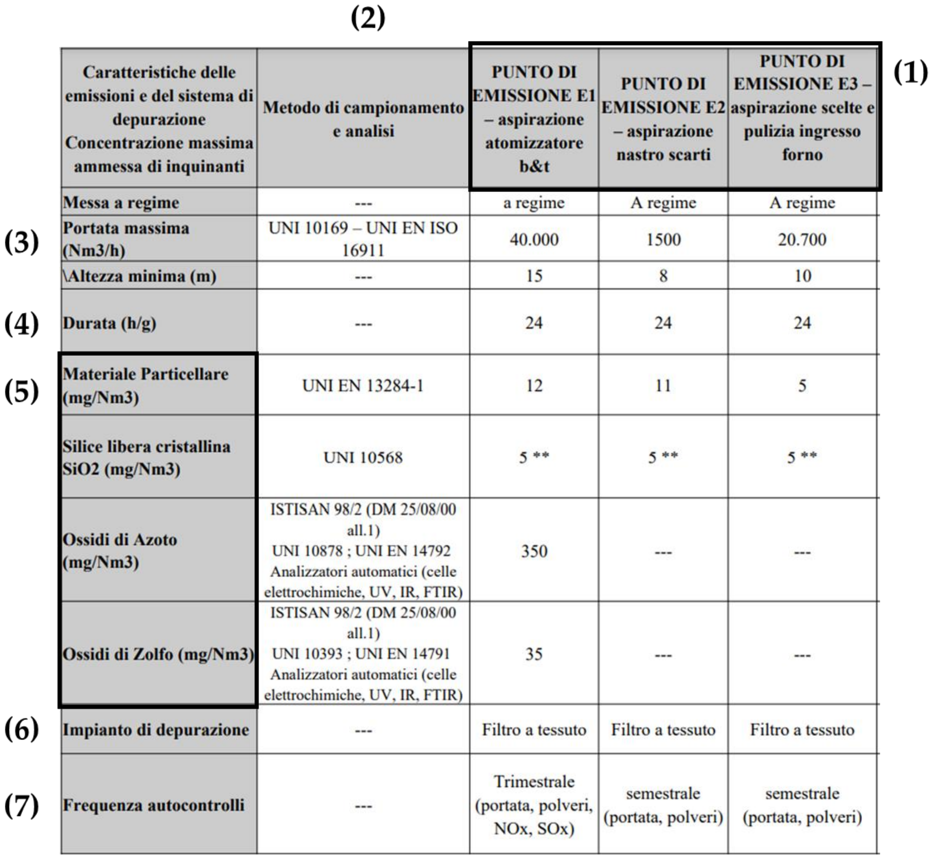
BAT-AEL		D.M. 29 Jan. 2007	BREF
Parameter	**Process**	**(mg/Nm^3)**	
Dust	General*	30*	1-10**
	Drying	30	1-20
	Spray drying	30	1-30
	Spray glazing	10	1-10
	Firing	5	1-5
HF	Firing	5	1-5
Pb	Firing	0.5	
VOCs	Firing	50	
Aldehydes	Firing	20	
NO$_x$	Firing		250
SO$_x$	Firing		< 500***
			(%)
Re-use of processed water	Whole manufacturing process	50	50-100
Re-use of sludge	Ceramic body preparation		0.4-1.5

(*) The BAT-AEL is related to the milling and pressing stages

(**) The BAT-AEL is related to all dusty operations

(***) BAT-AEL related to sulfur content of raw materials ≤ 0.25 %

The regional ARPA bureaus can accord to industrial installations permit conditions enacting the suggested emission limits, as stated inside the CER BREF, or different ones, often more rigorous, according to local specific environmental backgrounds. Usually, AIA documents can require additional limits for other pollutants, as crystalline silica, and contain all information regarding the control of pollutants for each source of emission within the installation. As an example, in **Figure 2-9** is reported an abstract of the atmospheric emissions chapter from an AIA document related to a porcelain stoneware tiles manufacturing unit in Italy.



Caratteristiche delle emissioni e del sistema di depurazione Concentrazione massima ammessa di inquinanti	Metodo di campionamento e analisi	PUNTO DI EMISSIONE E1 – aspirazione atomizzatore b&t	PUNTO DI EMISSIONE E2 – aspirazione nastro scarti	PUNTO DI EMISSIONE E3 – aspirazione scelte e pulizia ingresso forno
Messa a regime	---	a regime	A regime	A regime
Portata massima (Nm3/h)	UNI 10169 – UNI EN ISO 16911	40.000	1500	20.700
\Altezza minima (m)	---	15	8	10
Durata (h/g)	---	24	24	24
Materiale Particellare (mg/Nm3)	UNI EN 13284-1	12	11	5
Silice libera cristallina SiO2 (mg/Nm3)	UNI 10568	5 **	5 **	5 **
Ossidi di Azoto (mg/Nm3)	ISTISAN 98/2 (DM 25/08/00 all.1) UNI 10878 ; UNI EN 14792 Analizzatori automatici (celle elettrochimiche, UV, IR, FTIR)	350	---	---
Ossidi di Zolfo (mg/Nm3)	ISTISAN 98/2 (DM 25/08/00 all.1) UNI 10393 ; UNI EN 14791 Analizzatori automatici (celle elettrochimiche, UV, IR, FTIR)	35	---	---
Impianto di depurazione	---	Filtro a tessuto	Filtro a tessuto	Filtro a tessuto
Frequenza autocontrolli	---	Trimestrale (portata, polveri, NOx, SOx)	semestrale (portata, polveri)	semestrale (portata, polveri)

Figure 2-9. Abstract of an AIA document with reported authorized emission limits for different pollutants.

The numbers in **figure X** indicate:

(1) Emission point and related description
(2) Sampling and/or analysis methods
(3) Maximum permitted air flow
(4) Actual maximum working time
(5) Pollutants
(6) Filtering and/or purification devices
(7) Frequency of monitoring

The compliance of industrial installations to legal requirements is ensured through the publication of annual reports in accordance with the IED and accounting for all obligations as stated in each specific AIA documents. In addition, local authorities periodically operate inspection visits to production sites in order to collect information which are able to certify conformity to the environmental authorization in force.

2.7. EU ETS – Emissions Trading System

The EU ETS is the emissions trading scheme of the European Union, regulated through Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 (Directive 2003/87/EC, 2021). Similar schemes have been adopted among countries in order to control pollution and reduce greenhouse gases emissions. Born in 2005, the EU ETS was the first emissions trading scheme globally launched, currently covering around 45% of the EU's GHG emissions and 11.000 installations among the member states of the Union, plus Iceland, Liechtenstein and Norway (Environmental Protection Agency).

It is a market instrument with the aim of putting a cap on the GHG emissions of all participants and reducing emissions proportionally during each phase, or trading period, of the scheme, according to a "cap and trade system". The first trading periods covered the initial phase of the system, from 2005 to 2007, the second the period 2008-2012, the third 2012-2020, while the firth stretches from 2021 to 2030.

At the beginning of each phase, the cap of GHG emissions for each state is decided during the National Allocation Plan, supervised by the European Commission. The cap sets the number of possible delivered allowances, which is designed to progressively decrease of 1.74% each year, of 2.2% from 2018. Then, industrial installations are annually provided with a specific amount of allowances, which are basically rights to generate GHG emissions, corresponding to the permission to emit one equivalent ton of CO_2. At the end of the year, installations must return allowances according to the actual extent of CO_2 produced. If the number of allowances is excessed, then participants are forced to take action to reduce their emissions or matching the permit by buying the corresponding gap of allowances on the market. Allowances can be acquired from the market between installations or at auction from member states. The trading system allows parties to determine the right price for cutting emissions and to comply with the set cap, while the carbon price is decided by the market.

Two other flexibility mechanisms related to EU ETS are the Clean Development Mechanism (CDM) and the Joint Implementation (JI) which allow the implementation of projects aimed at reducing GHG emissions in other countries, as an alternative to a domestic reduction of emissions. Thus, companies obtain in exchange a number of credits equal to the amount of avoided tons of CO_2 related to the implementation of such projects. The actions of the Joint Implementation are limited to all those countries legally bind to emissions reduction, while projects from the Clean Development Mechanism shall be implemented in developing countries, which are not committed to an emissions trading scheme. Such practice has been devised to help countries in the global South to achieve a sustainable development and to boost economic growth while reducing at the same time emissions of greenhouse gases. In fact, many developing countries could not otherwise skip the high polluting phase of the industrial revolution related to oil and coal combustion, which would be economically profitable for them to lead economic growth at the pace of countries in the global North, but which would be obviously detrimental for the planet.

The EU ETS, as other emissions trading schemes, has been greatly welcomed among institutions, scientists and public opinion because is seen as a promoter of sustainable development, especially by boosting economic growth through long-term competitiveness. In addition, it is believed that the EU ETS can be of crucial importance for decarbonization and to stimulate investments in renewable energy technologies in Europe as well as around the globe.

Another part of the scientific and public opinion believes that such emissions trading schemes, especially through flexibility mechanisms as the Clean Development Mechanism, can negatively contribute to sustainable development by increasing existing inequalities among developed and developing countries and by not reducing actual amount of GHG emissions. In fact, the implementation of emissions-reducing projects in the global South is seen as a right to pollution for high polluting entities and, most of all, can corrupt the delicate equilibria in action among local communities in those countries (Böhm, Misoczky and Moog, 2012). As an emblematic example, it has been reported by Gilbertson, 2009 the case of a biomass energy plant in Thailand using rice husk as alternative raw material for power generation. Local farmers used to adopt such "waste" as natural fertilizer or as pore former in the manufacturing of bricks. Consequently, the implementation of such project has produced carbon credits and, thus, GHG emissions, while local communities have been deprived of a natural resource and compelled to convert to chemical fertilizers and to deal with the disposal of waste ashes from the biomass plant.

While opponents believe that more radical solution shall be undertaken for fighting climate change, sustainers believe that instruments as the emissions trading schemes can be beneficial for both the environment and economic growth, avoiding at the same time an excessive weight on society.

2.8. Waste management – European context

In the European context, waste management is regulated by Directive 2008/98/EC of the European Parliament and of the Council, known as Waste Framework Directive. It was recently amended by Directive (EU) 2018/851, through the addition of some definition of wastes and waste management practices (Directive (EU) 2018/851, 2018). Moreover, a revision of the Directive is currently underway, and it will be focusing on the most important policy areas of waste management, namely waste prevention and separate collection of wastes.

According to the Waste Framework Directive, waste management "*should be improved and transformed into sustainable material management, with a view to protecting, preserving and improving the quality of the environment, protecting human health, ensuring prudent, efficient and rational utilization of natural resources, promoting the principles of the circular economy, enhancing the use of renewable energy, increasing energy efficiency, reducing the dependence of the Union on imported resources, providing new economic opportunities and contributing to long-term competitiveness*" (Directive (EU) 2018/851, 2018). Briefly reassumed, wastes shall be managed without an additional negative impact on the society and the environment.

The main innovative introductions of the Directive 2008/98/EC are the polluter pays principle and the establishment of the waste hierarchy. According to the principle, the costs of the waste disposal shall be sustained by the producer of the product from which the waste derives or by present or previous holder of the waste. The partial or total responsibility of the producer of the product causing waste to pay for waste disposal will be resolved by Member States. As a result, most polluting and waste generating industries will be encouraged to waste prevention principally for economic reasons. In fact, besides an impaired business legitimacy, polluting companies will otherwise face high penalties.

On the other hand, the waste hierarchy helps industrial production to address efforts in waste management according to sustainability basis. It establishes an order of priority to waste disposal practices awarding those options able to deliver the best environmental outcomes. Thus, prevention is considered the most sustainable practice while disposal the least one, as illustrated in **Figure 2-10**.

Figure 2-10. Reversed pyramidal representation of the waste hierarchy, from disposal, which is the least sustainable practice, to waste prevention.

In fact, disposal of waste should be accorded only when no other practices are possible or whenever any other practice is considered more environmentally damaging or not economically practical.

In most of cases, especially for organic waste, are possible various energy recovery routes as the production of biogas or other types of bio-combustibles, of syngas ($CO + H_2$) through gasification, or simply the thermovalorization, which is the controlled incineration of waste for the generation of electricity. However, waste as glass, metal and ceramic are not suitable for energy recovery purposes and, if not properly managed, would be otherwise landfilled.

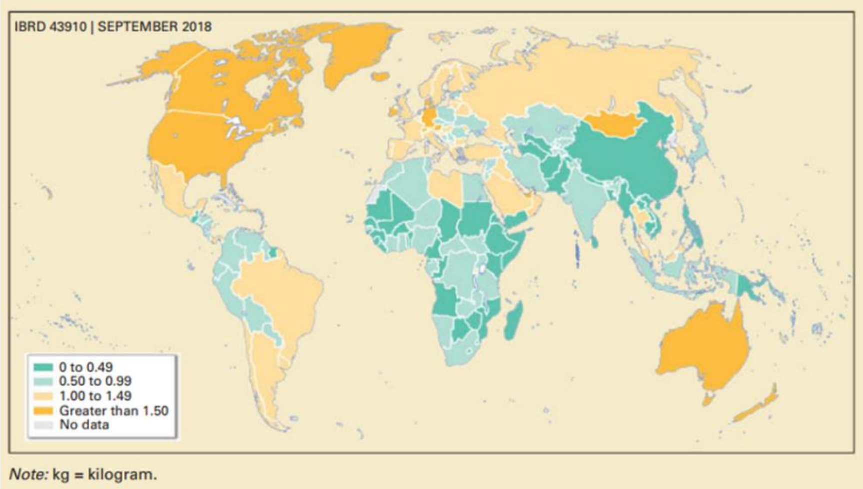
Therefore, all waste shall be preferably recycled or previously treated for recycling purposes. This waste management practice is more sustainable because the reutilization of materials can reduce exploitation of natural resources and costs related to raw materials extraction and processing. As an example, in the context of ceramics, the recycling of glass waste as flux inside the ceramic body or in substitution of frits in glazes and engobes compositions, reduces the adoption of natural occurring raw materials as feldspars and quartz and the energy expenditure related to frits synthesis. In the future, recycling and reutilization practices will be of primary importance not only for waste management but, especially, in the production and commerce of critical raw materials as the rare earths, extensively used in renewable energy production, in electric vehicles and in most technological devices (Massari and Ruberti, 2013).

Nonetheless, recycling of waste is often associated with a more or less relevant loss of material which must be consequently disposed of. For example, the valuable reutilization of metal components from secondhand vehicles does not include the valorization of all other non-metallic elements as fabrics, plastic and glass.

It is mainly for this reason that preparation for re-use is considered a more sustainable practice than recycling. In fact, the reutilization of the product after reparation or partial reconstruction will extend the whole life span of considered materials, granting after an additional utilization the same prospective for recycling or energy recovery.

The most sustainable practice of the waste hierarchy, however, is considered to be the prevention of waste. All those actions and policies which are able to prevent generation of waste are awarded with the highest grade of sustainability because prevent at the same time all possible negative impacts on environment and society related to just mentioned waste management practices.

In first place, waste prevention simply signifies to avoid excessive consumption of resources which will be afterwards turning into waste. As highlighted by the Directive 2008/98/EC, it is of imperative importance for the future sustainable development of human societies to change the current consumption patterns. In fact, the extreme consumption of resources to sustain the needs and lifestyles of society is not sustainable at current pace. The report from the World Bank Group "What a waste 2.0" of 2018, reports as 2.01 billion tonnes of municipal solid waste are globally generated each year and 33% of which is not managed in an environmentally safe manner (Kaza *et al.*, 2018). In addition, as revealed by Song *et al.*, 2015 almost one third of the food globally produced is not consumed and, thus, transformed in waste directly at the source. Data suggest as waste generation is not only unsustainable in terms of excessive mass production or environmental threats related to waste disposal, but as it is also not equally distributed on the planet, as illustrated in **Figure 2-11**.



Note: kg = kilogram.

Figure 2-11. Global waste generation per capita, from (Kaza *et al.*, 2018).

Higher income countries tend to produce more waste per capita respect to other areas of the world as the South Asia and sub-Saharan Africa. If current consumption patterns are not revised, in the future developing countries will be generating the same amount of waste as developed countries, resulting in the impossibility for the planet to bear such amount of waste and the related corruption of life on seas and lands and atmospheric pollution threats.

Secondly, waste prevention can be carried out through the rational design of products aimed at the reduction of resources consumption. In this sense, products shall be manufactured accordingly to best recycling practices and to allow an easy reutilization of different materials. For example, the increased efficiency of energy storage or energy production devices as lithium batteries or solar panels can reduce the amount of materials involved in the manufacturing of these products, contributing at the same time to decrease the generation of waste. Likewise, a rational design of electronic items or composite materials can support and boost recycling practices through a simpler disassembling and easier separation of different materials.

Nonetheless, it should be highlighted as the Directive 2008/98/EC states that delivering the most sustainable environmental outcomes does not always imply the uncompromising adherence to the waste hierarchy. On the contrary, it suggests as some specific waste streams may require to depart "*from the hierarchy where this is justified by life-cycle thinking on the overall impacts of the generation and management of such waste*" (Directive 2008/98/EC, 2008).

It is interesting to notice that waste prevention is not only the most environmentally sustainable practice of waste management, but it can be also economically profitable for industries. In fact, the generation of waste from the producer standpoint is a manifestation of the incomplete and inefficient utilization of resources. In this regard, all the potential value of raw materials is not completely transferred to final products, resulting in a loss of profit. Even if waste are sold to third parties for recycling or if, conversely, are reintroduced inside the same production process, the recycling of materials always results in additional energy expenditure and/or in loss of material. Considering two examples from the ceramic tile industry, it has been reported as the recycling of fired scraps often requires a preliminary milling treatment, which is a cost for factories, and even the reutilization of unfired tiles residues involves a whole series of collecting operations and results, in the end, in an increased energy expenditure for pressing devices (Busani, Palmonari and Timellini, 1995).

Such considerations are in line with the hypothesis of the economist M. E. Porter, among the first to emphasize the double benefit of environmental regulations (Porter and van der Linde, 1995). According to Porter, even strict environmental policies, besides the inherent benefits related to protection of the natural ecosystem, are able to promote the necessary industrial innovation which, in turn, will bring to overall economic benefits by delivering profits greater than the actual expenditure for complying with the environmental regulations. In fact, in the perspective of a future sustainable development, the industrial competition will not be played on minimizing the costs of production means and work force but, rather, on delivering the best sustainable outcomes to manufacturing processes.

2.9. Waste management - Italian ceramic tile sector

Among Italian ceramic tile factories, the waste management is regulated according to Italian decree D. Lgs. of 2 December 2010 n° 205, adopting European Directive 2008/98/EC (*D. Lgs. 3 Dicembre 2010, n. 205*). As it happens for the industrial emissions control, all the procedures regarding waste management are reported inside the AIA document for each specific industrial installation.

Waste are labelled according to specific codes and qualified according to hazard, solid state and destination. Then, waste are transferred to third parties for recycling or landfilling purposes.

Wastewaters are normally recycled internally to manufacturing plants while rainwaters are directed through collecting points where can be reintroduced inside the production process or simply discharged into water streams. In fact, the contact between rainwater and other materials is inhibited because waste, raw materials and finished products are always secured in indoor warehouses or protected by waterproof shelters and/or packaging.

European Commission Decision 2000/532/EC, also known as the European Waste Catalogue (EWC), presents a list of waste providing a standard framework useful for identification of different waste sources and for data comparison across all member states. Individual wastes are designated with a six-digit code, of which the first two digits representing the chapter of the catalogue, the next two the subchapter and the last two the waste type (*2000/532/EC*, 2000). In **Table 2-3** are illustrated the EWC codes (CER in Italian; *Catalogo Europeo dei Rifiuti*) corresponding to the principal waste sources of ceramic tile manufacturing.

Table 2-3. CER codes of main waste of the production process of ceramic tiles.

CER code	Waste origin
	Chapters
08	**Wastes from the manufacture, formulation, supply and use (MFSU) of coatings (paints, varnishes and vitreous enamels), adhesives, sealants and printing inks**
10	**Inorganic wastes from thermal processes**
	Sub-Chapters
08 02	**Wastes from MFSU of other coatings (including ceramic materials)**
10 12	**Wastes from manufacture of ceramic goods, bricks, tiles and construction products**
	Wastes
08 02 02	aqueous sludges containing ceramic materials
08 02 03	aqueous suspensions containing ceramic materials
10 12 01	waste preparation mixture before thermal processing
10 12 08	ceramic scraps after thermal processing
10 12 09*	solid waste from gas treatment, containing hazardous substances
10 12 99	waste not otherwise specified

The waste with CER code 10 12 09*, that is exhausted lime coming from flue gas treatment, is labelled as hazardous waste, as identified by the asterisk (*), and it is subject to the provisions of Directive 91/689/EEC on hazardous waste (Council Directive 91/689/EEC, 1991).

All other wastes are recycled or transferred to third parties for recycling purposes. In fact, as it will be shown in the **section 3.4** of results and discussion, almost the entirety of waste produced from the manufacturing process of porcelain stoneware tiles is reinserted inside the same process or, otherwise, is transported for recycling to bigger ceramic factories or, again, to other parties belonging to different industrial sectors.

3. Results and discussion

3.1. Atmospheric emissions – Sampling procedures and analytic methodologies

In this chapter a description of the procedures for the collection of environmental data and for the chemical analysis is provided.
Environmental samples have been collected from year 2019 to year 2022 directly at the emission points of industrial installations. Then, at *Centro Ceramico* the analysis of certain pollutants from the collected specimens and the data management for the obtainment of the ultimate analytic results took place. These results were communicated to companies, which subsequently uploaded them in the form of environmental reports on the public web portal of ARPAE, becoming publicly accessible (*Homepage - Autorizzazione Integrata Ambientale - Regione Emilia Romagna*). It was these data, submitted anonymously, that were used for the data analysis presented in the next sections, with the aim of describing the sustainability and environmental impact of the Italian ceramic tile sector. The author contributed to collect only a minor fraction of the enormous quantities of single determinations that were used for the following discussion on atmospheric emissions and waste management practices. The data analysis was conducted by making use of software InProCer, developed for *Centro Ceramico* for this specific purpose, which allow the extraction of information from the environmental reports, and then through Microsoft Excel 2019, which was used to formulate emission factors and other environmental performance indicators presented in the following sections.

The environmental sampling campaigns in which the author of this thesis took part involved the assessment of the following pollutants: particulate matter, fluorine compounds (reported as HF), lead, nitrogen and sulfur oxides (NO_x and SO_x), volatile organic compounds (VOCs), aldehydes, heavy metals and crystalline silica. As a total, 396 singular determinations of pollutants were performed by the author among principally 4 ceramic tile factories. Distribution of sampling by pollutants is illustrated in **Figure 3-1**.

Pollutants	N° of samplings	Total percentage (%)
Particulate matter	186	47.0
HF	48	12.1
Lead	32	8.1
NO_x and SO_x	68	17.2
VOCs	18	4.5
Aldehydes	18	4.5
Heavy metals	18	4.5
Crystalline silica	8	2.0
Total	396	100

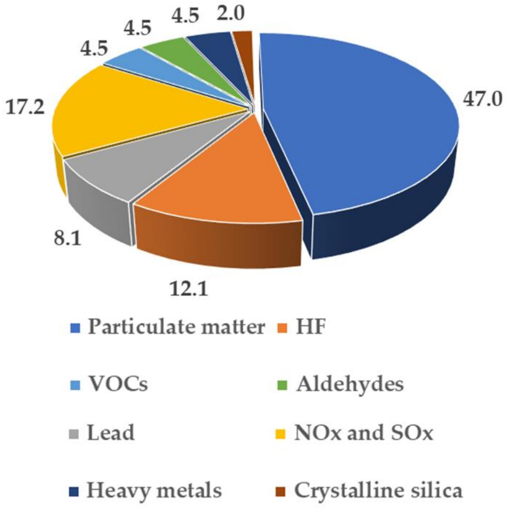


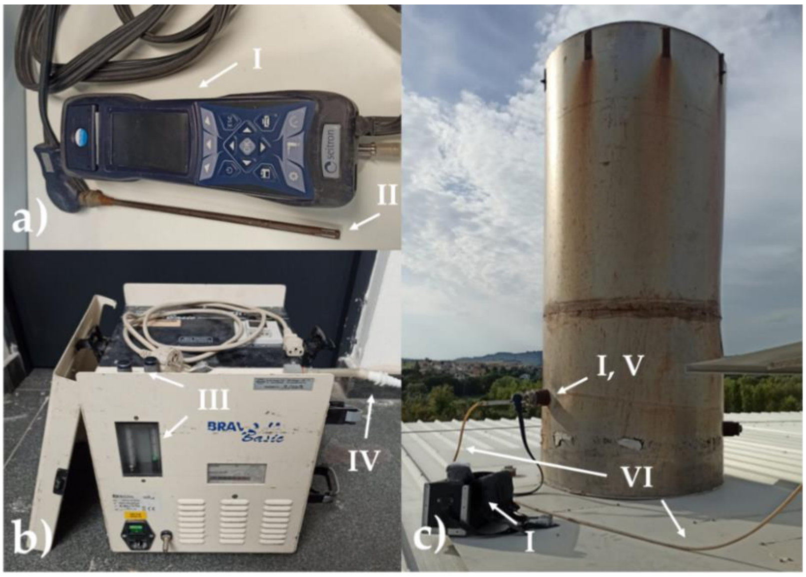
Figure 3-1. Summary of the number of performed samplings and related percentage representation by pollutants.

The greatest percentage of environmental samplings is represented by particulate matter and mainly because the determination of this kind of pollutant is requested for basically each emission point within each ceramic tile factory. On the other hand, the quantification of the second and third most sampled pollutants, that are nitrogen and sulfur dioxide and, after, fluorine compounds, are required only for the spray-drying equipment and kilns and not for other stages not involving high temperatures. The same applies for lead, volatile organic compounds, aldehydes and heavy metals. Crystalline silica, on the other hand, is normally rarely required to companies, even if it is theoretically strictly related to particulate matter as pollutant. In this specific case, the determination of crystalline silica was demanded by only one AIA document for each emission point of a singular ceramic factory.

The sampling procedure of atmospheric emissions starts with the measure of the flow rate inside the gas conduct of the emission point. The sampling section should be located far from previous bending points, in order to measure a stable flow, and preferably near the end of the conduct, to retain the conditions of the gases at the exact moment of emission. Two examples of emission conducts are illustrated in **Figure 3-2**, where the sampling hole has been highlighted in red.

Figure 3-2. Example of two emission conducts from ceramic tile factories. Red circles highlight the sampling hole.

Measuring the gas flow rate is necessary because each emission point, besides being subjected to emission limits, is also regulated according to specific thresholds of flow rate and working hours reported inside the AIA documents that cannot be exceeded. In addition, some pollutants, as particulate matter, lead and heavy metals, are required to be sampled under isokinetic flow conditions. Isokinetic sampling occurs when the velocity and direction of the gas entering the sampling nozzle are the same as the velocity and direction of the gas in the duct at the point of measurement. The collection of air samples was performed using a portable flow rate sampler Tecora Bravo Basic connected with silicon tubes to the sampling hole of the emission points and using a Seitron Chemist 600 portable gas analyzer to check the O_2 and CO_2 concentration and temperature values of the emission gases, as illustrated in **Figure 3-3**.



I. Gas analyzer

II. Thermocouple and gas sampling gun

III. Air flow intake speed regulation

IV. Air flow intake conduct

V. Sampling probe

VI. Silicon tubes

Figure 3-3. Portable gas analyzer **a)**, flow rate sampler **b)** and sampling configuration on an emission conduct of a ceramic tile factory **c)**, with corresponding enumerated description of components.

The sampling and analytical procedures related of each specific pollutant are described below.

Flow rate

The flow rate inside the gas conduct of the emission point was determined according to standard UNI 10169:2001 using a micromanometer MA 202 Ceramic Instruments and a classic Pitot tube (*UNI 10169:2001 - UNI Ente Italiano di Normazione*, 2001).

Particulate matter

Particular matter was sampled under isokinetic conditions according to standard UNI EN 13284-1:2017 (*UNI EN 13284-1:2017 - UNI Ente Italiano di Normazione*, 2017). Adherence to isokinetic conditions allows the collection of a dust sample that is representative of the concentration inside the emission conduct and is neither greater nor lesser, as would be the case at different suction rates. This happens because, unlike gaseous pollutants, particulate material and all other related pollutants are present in solid form. The sampling was carried out by using a metal probe with glass fiber and a calcium silicate fiber filter as a trap for particulate matter particles (**Figure 3-4**).

Figure 3-4. Components of a particulate matter probe with 3-, 4-, 6-, 8- and 12-mm nozzles (left) and sampling metal case with glass fiber and calcium silicate fiber filter (right).

The determination of the quantity of particulate matter (mg) was carried out through gravimetric analysis, calculating the total weight of the metal case after sampling and subtracting it from the tare weight.

Fluorine compounds

Fluorine compounds were sampled according to standard ISTISAN 98/2 (D.M. 25/08/00 Annex 2) (*ISTISAN 98/2 (DM 25/08/00 Allegato 2)*).

Sampling was performed by bubbling the gas at a 0.5 L/min rate for 60 minutes through three bubbler containing 30 mL each of 0.1 M sodium hydroxide solution, with the purpose of trapping the acidic fluorine species in ionic form. Afterwards, the determination of the quantity of fluorine compounds (in the form of fluorine acid, HF), was carried out through ionic chromatography using a Metrohm 761 Compact ionic chromatograph. Knowing the volume of the sodium hydroxide solution it was possible to obtain the corresponding quantity of fluorine acid (mg).

Lead

Lead compounds were sampled according to standard UNI EN 14385:2004 (*UNI EN 14385:2004 - UNI Ente Italiano di Normazione,* 2004).

Particulate matter samples, after the gravimetric analysis, were subjected to acidic digestion with a 70% nitric acid solution. After acid digestion and removal of residual acid by evaporation, the solid was solubilized with 10 mL of a 5% nitric acid solution and submitted for chemical analysis using a Perkin Elmer Optima 3200 XL ICP optical emission spectrometer.

Nitrogen and sulfur oxides

Nitrogen and sulfur oxides (NO_x and SO_x) followed the same sampling procedure, and were sampled according to standard ISTISAN 98/2 (D.M. 25/08/00 Annex 1) (*ISTISAN 98/2 (DM 25/08/00 Allegato 1),* 1998).

Sampling was performed by bubbling the gas at a 0.3 L/min rate for 60 minutes through three bubbler containing 30 mL each of a 0.025 M potassium permanganate and 1.25 M sodium hydroxide solution, with the purpose of trapping the nitrogen and sulfur species in their oxidized form inside the solution, according to the following reactions:

$$2MnO_4^- + 3SO_3^{2-} + H_2O \rightarrow 3SO_4^{2-} + 2MnO_2 + 2OH^-$$

$$2MnO_4^- + 3NO_2^- + H_2O \rightarrow 3NO_3^- + 2MnO_2 + 2OH^-$$

After the sampling, the collected solution was let reacted with a 30% hydrogen peroxide solution in order to completely consume the excess of potassium permanganate. The excess of hydrogen peroxide was eliminated through mild heating of the solution. Afterwards, the determination of the corresponding nitrates and sulphates was carried out through ionic chromatography using a Metrohm 761 Compact ionic chromatograph. Knowing the volume of the potassium permanganate/sodium hydroxide solution it was possible to obtain the corresponding quantity of nitrogen and sulfur oxides (mg), expressed as NO_2 and SO_2, respectively.

Otherwise, the determination of nitrogen and sulfur oxides was performed by using a Seitron Chemist 600 portable gas analyzer, which directly furnished concentration values of mentioned gases (mg/m^3).

Volatile organic compounds

Volatile organic compounds (VOCs) were sampled according to standard BS EN 12619:2013 (*BS EN 12619:2013*).

The determination was performed by using a Pollution Polaris SE flame ionization detector, which directly furnished concentration values of volatile organic compounds inside flue gas (mg/m^3).

Aldehydes

Aldehydes were sampled according to standards EPA TO11A and NIOSH 2541 (*EPA Method TO11A; NIOSH 2541, Issue 2,* 1994).

Sampling was performed at 0.5 L/min rate for 30 minutes, adsorbing flue gas on a 2,4-diphenylhydrazine vial. Determination of chemical species was carried out through HPLC analysis by an external laboratory.

Heavy metals

Heavy metal compounds were sampled according to standard UNI EN 14385:2004 (*UNI EN 14385:2004*).

The sampling and analysis procedures followed the same steps as in the case of lead compounds.

Crystalline silica

Crystalline silica was sampled under isokinetic conditions according to standard UNI 10568:1997 (*UNI 10568:1997*).
The determination of the amount of collected powder was determined by gravimetric analysis while the presence of crystalline phases was carried out through XRD diffractometry using a Panalytical Empyrean diffractometer equipped with a CuKα tube (1.5406 Å) operating at a voltage of 40 kV and using a current of 30 mA.

Once the quantity (g or mg) of the above-mentioned pollutant was determined, it was possible to express values as mg/Nm^3, by knowing the flow rate of each emission point, or as mg/m^2, by knowing both the contribution for each emission point to the total emission flow rate authorized to the factory and the total tile production in square meter reported for the same industrial installation. These two were the main units in which emissions were reported in the following sections.

Data regarding heavy metals and crystalline silica have not been reported because of the scarcity of available information from the environmental reports delivered by companies. However, it is necessary to point out that this scarcity is due to the absence of a mandatory determination of these pollutants in most of the environmental permits (AIA documents) issued by the relevant authorities to ceramic tile factories.

Concluding remarks on sampling procedures and analytic methodologies

The data collected by the author himself during the environmental sampling campaigns were not reported separately but, to the contrary, displayed in conjunction with data provided by the Emilia-Romagna region (ARPAE), which were obtained as a result of different sampling campaigns performed by third parties. This methodology was considered the most faithfully describing the real process of data collection upon which legal limits are discussed and revisions of environmental directives are implemented. In fact, considering the enormous amount of data needed to describe the environmental performance of an entire industrial sector, it would have been inappropriate to demand a perfect reproducibility for the whole sample of data as, for example, if these were being obtained following a unique sampling technique performed by the same operator in the same environmental conditions. For this reason, it shall be reminded here that every single data carries with it some uncertainty, whose evaluation was beyond the scope of this thesis. On the contrary, what is of paramount importance is the overall trend of data, capable of showing the ultimate values of performance indicators and the increasing or decreasing trends these indicators manifested over the years.

Actually, even assuming the consistency of sampling procedures, it shall be noted as the existing conditions in which environmental samples are usually collected are hardly found consistent. Factors that are difficult to control in actual sampling campaigns include the nature and flow of production at the time of sampling, the occurrence of issues such as downtimes during sampling, the production of special products, weather events that may increase or decrease the presence of pollutants (*e.g.*, wind during sampling of particulate matter), the state of preservation of industrial chimneys and filters, communication problems with company's employees and other factors that are difficult to foresee. However, through the repetition of sampling at the same plants during the year, along with the large amount of data available, it is possible to mediate the fluctuations that may occur as a result of individual sampling to provide a true and faithful representation of the environmental performance of this industrial sector. Finally, it is suggested that above all, a constant, rather than a spot measurement of pollutants, would be the best way to ensure the most faithful possible representation of such performance.

3.2. Evolution of atmospheric emissions from the Italian ceramic tile sector

One of the most important activity carried out during the present PhD project has been the study of the evolution over time of the atmospheric emissions from the Italian ceramic tile sector.

Together with the ceramic district of *Castellón* (Valencia), in Spain, the area stretching over the municipalities of *Sassuolo* and *Fiorano Modenese* (Modena), in Italy, is characterized by a high density of ceramic tile manufacturers and represents one of the biggest ceramic districts in Europe. Due to such high concentration of industrial installations, the air quality in those areas has been negatively affected in the past. As a result, both industrial associations and national institutions started to devote particular attention to the problem of environmental pollution and to develop an important awareness toward the sustainability of the production processes (Minguillón *et al.*, 2007, 2009, 2013).

A wide number of scientific studies and analytical surveys have been issued over the years concerning the air quality and the assessment of the environmental conditions affecting the pollution levels in those areas. In 1978, as a consequence of a major investigation into the climatic conditions of the area, it was possible to correlate the concentration of certain pollutants found at ground level with the nature and extent of atmospheric emissions from surrounding factories (Palmonari, 1979). This made it possible to determine appropriate emission limits for these pollutants to ensure better air quality standards.

Since then, industrial emissions related to the ceramic tile sector have been continuously monitored and the environmental performance of factory regularly disclosed and discussed (Busani *et al.*, 1995; Assopiastrelle, 1998; Resca *et al.*, 2021; Timellini *et al.*, 2008).

The present assessment stands as a perpetuation of these studies. In addition, it can help to shed light on the weaknesses in production processes, highlighting possible areas of action for the continuous improvement of the environmental conditions in the Italian ceramic district and of the sustainability of this important industrial sector.

In this work, a vast quantity of data was collected among Italian ceramic tile manufacturers with the aim of illustrating the evolution trends for the atmospheric emissions related to industrial production. The actual emission trends were discussed and, when possible, compared with the standards associated to the best available techniques at national and international level, represented correspondingly by the ones stated inside the Italian decree D. M. of 29 January 2007 and in the EU Hard Coverings Ecolabel (Commission Decision (EU) 2021/476 of 16 March 2021; *D. M. 29 Gennaio 2007*).

3.2.1. *Methodology of data collection and analysis*

Data have been collected from around 90 ceramic tile manufacturers located in the Emilia-Romagna region (Italy), starting from 2010 and with little but constant fluctuations in the number of factories in the sample, from a minimum of 84 (2014) to a maximum of 91 (2010) industrial installation considered over the time period (2010-2019) (Resca *et al.*, 2021). Such inconstancy is related to the different sample of ceramic factories delivering their environmental reports each year with the aim of contributing to similar research studies. However, because of the high number of data and the high similarities between both the manufacturing processes and final products, represented in this case almost entirely by porcelain stoneware, small fluctuations in the sample were deemed acceptable for the present discussion.

The data collection and the resultant assessment have been performed in collaboration with the association of ceramic manufacturers *Confindustria Ceramica* and the Emilia-Romagna region.

The pollutants considered were those characteristic of the manufacturing process of ceramic tiles, that are particulate matter (PM), fluorine compounds (F^-), lead (Pb) volatile organic compounds (VOCs) and aldehydes, nitrogen oxides (NO_x) and carbon dioxide (CO_2). Sulfur oxides (SO_x) were not considered because of the scarcity of data.

The sampling methods of all the above-mentioned pollutants were accessed from the AIA documents and reported below:

- Particulate matter (PM): *BS EN 13284-1,* 2017; *UNI EN 13284-1:2003*
- Fluorine compounds (F^-): *ISTISAN 98/2 (DM 25/08/00 Allegato 2); UNI 10787:1999*
- Volatile organic compounds (VOCs): *BS EN 12619:2013; UNI EN 13526:2002; UNI EN 13649:2002*
- Aldehydes: *EPA Method TO11A; NIOSH 2539, Issue 2,* 1994; *NIOSH 2541, Issue 2,* 1994
- Lead compounds (Pb): *ISTISAN 88/19; UNICHIM 723/1986; UNI EN 14385:2004*
- Nitrogen oxides (NO_x): *BS EN 14212:2012; BS EN 14792:2006; ISTISAN 98/2 (DM 25/08/00 Allegato 1); UNI 10878:2000*
- Sulfur oxides (SO_x): *BS EN 14212:2012; BS EN 14791:2006; ISTISAN 98/2 (DM 25/08/00 Allegato 1); UNI 10246-1:1993*.

The data were used to obtain environmental indicators capable of describing the emission performance of the ceramic tile sector during the period of analysis.
In particular, emission factors (EF) were designed for each pollutant (*i*) according to the following equation:

$$EF_i \text{ [mg/m}^2\text{] or [g/m}^2\text{]} = \frac{\sum_{k=0}^{k=n} EFs_{i,k} P_k}{\sum_{k=0}^{k=n} P_k}$$

where *n* is the number of factory of the sample for each year; EFs_i [g/m^2] is the emission factor for the *i*-pollutant registered for the *k*-factory; and P_k [m^2/year] is the total annual production of the *k*-factory. The specific emission factors EFs_i were included in the environmental reports delivered by factories, calculated according to the following equation:

$$EFs_i \text{ [g/m}^2\text{]} = \frac{MF_i}{P * 1000}$$

where MF_i [kg/year] is the mass flow for each *i*-pollutant, calculated according to the actual annual working hours and air flow of each plant inside factories; and P [m^2/year] is the total annual production of ceramic tiles.
The EFi represents the amount of the *i*-pollutant emitted per square meter of tile

manufactured. In this sense, the emission factors can faithfully describe the environmental performance of companies because independent to the individual productive dimensions of each industrial installation.
In the case of EU Ecolabel, the excellence environmental thresholds have been chosen as reference limit and converted from mg/kg to g/m^2 of final product based on a medium weight of 19.9 kg/m^2 (as declared in the ceramic tile EPD) for the purpose of a proper comparison.

For the purpose of the present assessment, all emission factors were subdivided according to three different production classes described as follows:

- Class 1: complete manufacturing process (as depicted in **Figure 3-5**);
- Class 2: complete manufacturing process and additional production of spray-dried powder for third parties;
- Class 3: partial manufacturing process, not involving the production of spray-dried powder and all the stages ahead.

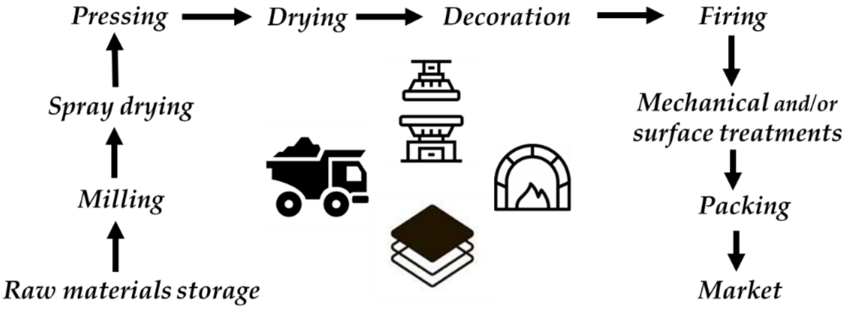


Figure 3-5. Schematic representation of the manufacturing process of ceramic tiles.

This subdivision was necessary in order to compare those ceramic factories displaying the same characteristics and to avoid evaluation errors due to substantial differences between the above-mentioned types of production layouts. Actually, there are also factories that exclusively produce powder and supply those to ceramic tile producers. The environmental reports of this type of plant were not included in the data collection provided by the Emilia-Romagna region and, therefore, could not be taken into account.
Figure 3-6 reports the number of ceramic tile factories for each of the three classes. Class 1 is the least represented one, displaying a number of plants ranging between 16 and 21. Class 2 and 3 are by far more represented, the latter including a higher number of factories than the former one. Even if representation with each class has been more or less constant during the year, the lower number of industrial installations belonging

to class 1 could have led to a lower level of consistency in the emission factors of such class.

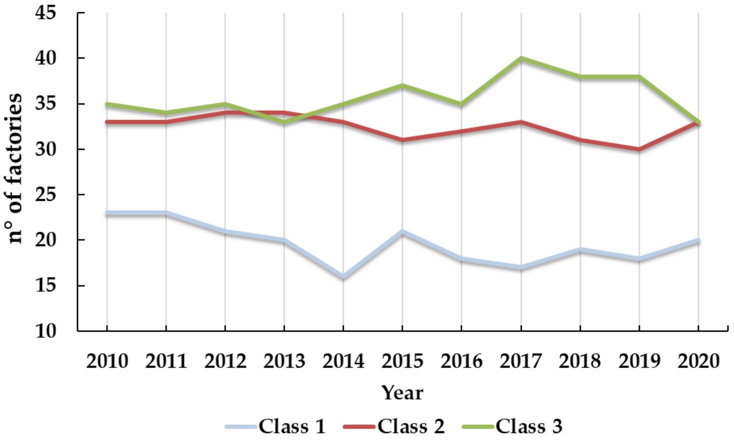


Figure 3-6. Number of ceramic factories represented by the three production classes for the period 2010-2020.

Finally, it shall be highlighted here that the industrial production has been strongly impacted in Italy during 2020 by reason of the COVID-19 pandemic. Thus, the emission factors of pollutants for that year, calculated as mentioned using data concerning the total production and atmospheric emissions, have been surely affected accordingly.

3.2.2. *Atmospheric emission of particulate matter*

The collected data cover a time period of eleven years, from 2010 to 2020 for all the pollutants considered in the present study. However, the emission factors for particulate matter (PM), fluorine compounds (F^-) and lead (Pb) have been developed on a longer time span, including also available data from the three-years period 2005-2007, which had to be considered together. Furthermore, data dating back to the late 1990s were also reported for the same pollutants but could not be broken down into the three categories and, therefore, it was decided not to include them in the graphs.

In **Figure 3-7**, the trend for the emission factor of particulate matter (EF_{PM}), representative of the Italian ceramic tile sector, is reported over a time span of fifteen years.

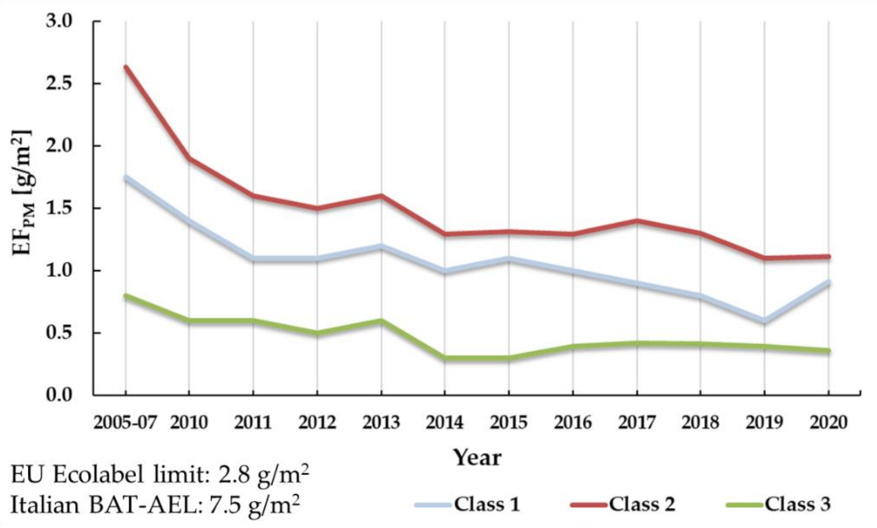


Figure 3-7. Emission factor of particulate matter (EF_{PM}), represented from year 2005 to 2020, according to the subdivision in the three production classes.

It is reported in the literature as the value of emitted particulate matter calculated as a mean for the whole Italian ceramic tile sector in the years 1996-1997 was around 4.4 g/m^2 (Assopiastrelle, 1998). Thus, the trend of EF_{PM} significantly decreased along the years, especially until 2014, where values more or less stabilized around 1.30 and 0.35 g/m^2 for class 2 and 3, respectively, while values regarding class 1 continued to decrease up to a minimum of 0.6 g/m^2 in 2019.

Both the emission level associated with the best available techniques in force in Italy, equal to 7.5 g/m^2, as the EU Ecolabel limit of 2.8 g/m^2 are met to a large margin, being the highest registered value during the last four years equal to 1.41 g/m^2, scored by class 2 in 2017. Such values demonstrate that there is high concern regarding the containment of particulate matter among manufacturers and that the most optimized abatement technology is being currently adopted within ceramic tile factories.

Moreover, it is easy to see how the three production classes progressively decrease while always showing a similar ratio between them. This fact is related to the distinct flow of raw materials that factories belonging to a specific production class have to deal with. In fact, factories belonging to class 2, because of the excess production of spray-dried powder, manage higher quantities of raw materials for the same square meters of tiles manufactured, in comparison to class 1 and 3. In particular, these latter are free from the input of particulate matter coming especially from the spray-drying stage and from all stages ahead. On the other hand, factories represented by class 1 rank in the middle, as it would be expected.

3.2.3. *Atmospheric emission of fluorine compounds*

In **Figure 3-8**, the trend for the emission factor of fluorine compounds (EF_{F^-}), representative of the Italian ceramic tile sector, is reported over a time span of fifteen years.

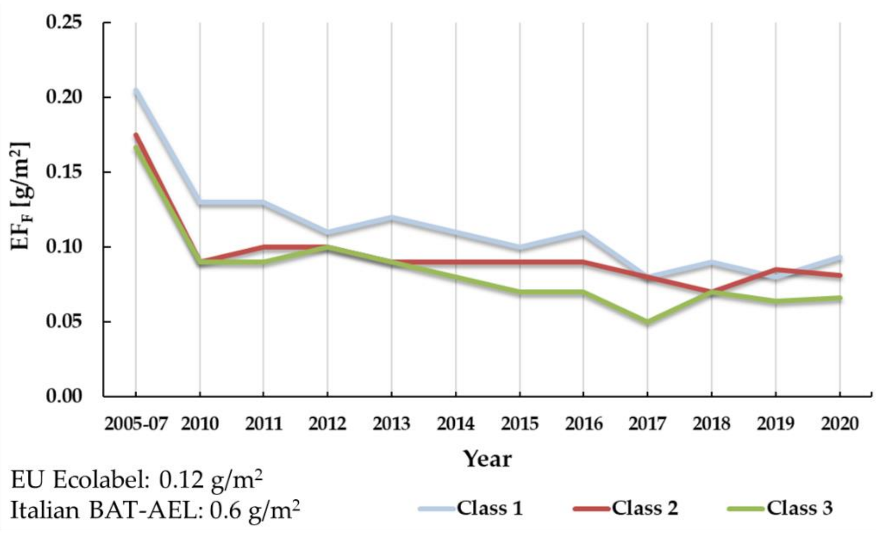


Figure 3-8. Emission factor of fluorine compounds (EF_{F^-}), represented from year 2005 to 2020, according to the subdivision in the three production classes.

Th reported value of the emission factor for the two-years period 1996-1997 was equal to 0.48 g/m^2 (Assopiastrelle, 1998). Then, starting from 0.20, 0.18 and 0.165 g/m^2 registered in 2005-2007, values progressively decreased over time, reaching a minimum of 0.05 g/m^2 for class 3 in 2017, of 0.082 g/m^2 for class 1 in 2019 and of 0.07 g/m^2 for class 2 in 2018. However, over the last three years, the emission factors of all three production classes seem to have stabilized in the range 0.06-0.08 g/m^2.

Differently from the case of particulate matter, the values registered for the emission factor of fluorine compounds are more similar to each other, suggesting that this pollutant is not so strictly related to the different production layouts presented here. In fact, as previously mentioned in **section 1.4**, the emission of fluorine is a peculiar characteristic of the firing process, as a reason of the high temperatures involved in this stage. Because all three classes display such stage, there are not significantly differences in the emission factors registered during the years.

Finally, it shall be noticed as the comparison of the current stable trend with the emissions thresholds stated by the EU Ecolabel and the Italian best available techniques (respectively equal to 0.12 and 0.6 g/m^2), demonstrate the important efforts made by the Italian ceramic tile sector in the containment of fluorine emissions both within the national and international context.

3.2.4. *Atmospheric emissions of lead (Pb)*

In **Figure 3-9**, the trend for the emission factor of lead (EF_{Pb}), representative of the Italian ceramic tile sector, is reported over a time span of fifteen years.

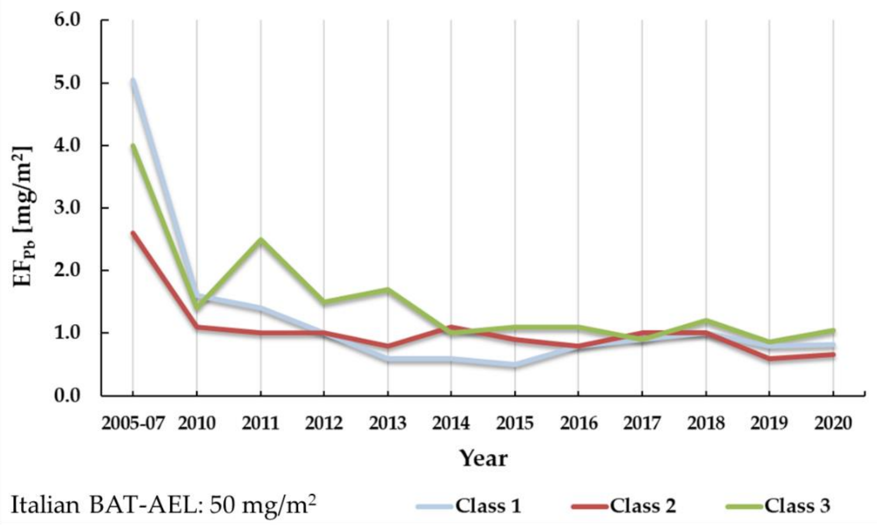


Figure 3-9. Emission factor of lead (EF_{Pb}), represented from year 2005 to 2020, according to the subdivision in the three production classes.

In this case, it was found that the value registered in the late 1990s was over 100 mg/m^2 (Assopiastrelle, 1998). Such concentration is easily justified by the extensive use of lead oxides inside ceramic glazes, an additive able to enhance the gloss and the overall aesthetic appearance of ceramic decorations. During the three-years period from 2005 to 2007, values were quite high (5.1, 4.0 and 2.6 mg/m^2, for class 1, 2 and 3 respectively) if compared to the current stable trend. In fact, it seems that starting from 2014 the emission factor of lead has been stabilizing, with minor exceptions, around a strict range of 0.6-1.0 mg/m^2.

It is suggested here as the choice for alternative and safer oxides inside ceramic glazes, as well as the introduction of the digital ink-jet decoration technology, have certainly contributed to the almost complete eradication of lead from the manufacturing processes of ceramic tiles.

The success in the elimination of this element from the ceramic tile sector is highlighted by the comparison with the emission level (50 mg/m^2) associated to the Italian best available techniques. On the other hand, the EU Ecolabel legislation does not consider any emission limit for lead. This probably means that the Italian BAT should be revised and updated to the current level of technology, which does not take into consideration lead compounds as characteristic pollutants related to the ceramic tile industry anymore.

3.2.5. Atmospheric emission of volatile organic compounds (VOCs)

In **Figure 3-10**, the trend for the emission factor of volatile organic compounds (EF_{VOCs}), representative of the Italian ceramic tile sector, is reported over a time span of eleven years.

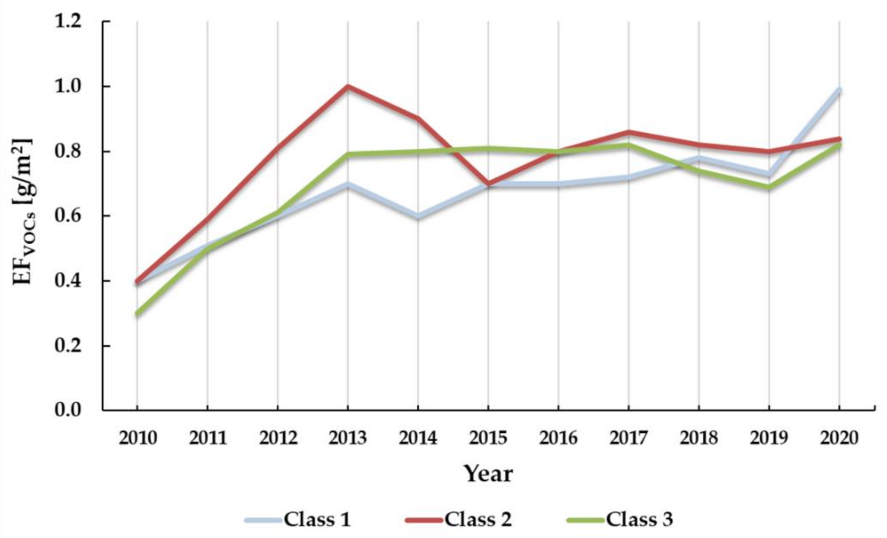


Figure 3-10. Emission factor of volatile organic compounds (EF_{VOCs}), represented from year 2010 to 2020, according to the subdivision in the three production classes.

As previously mentioned, the atmospheric emissions of volatile organic compounds (VOCs) are related to various factors. In particular, the chemistry of the additives added to ceramic suspensions, the use of organic solvents in ceramic inks for the ink-jet decoration technology, the adoption of a post-combustion equipment and the oxidant or reductive atmosphere inside kilns can all play a crucial role in the emission of organic pollutants from the firing process. Especially, the change in the market requirements caused by the abandonment of lead-containing glazes and by the introduction of the digital decoration technology, besides motivating a progressive change in the market requirements, have also induced a significant substitution of the characteristic pollutants historically linked to ceramic decoration.

For these reasons, it is not surprising that while emissions related to lead compounds have been progressively decreasing since 2005, the emission factor of volatile organic compounds has continuously raised from 2010 to 2013, when scored a maximum value of 0.6, 0.9 and 0.8 g/m^2, for class 1, 2 and 3, respectively. After that point, values decreased and stabilized around a range of 0.75 g/m^2. It is only in the year 2020 that the emission factors increased noticeably. Especially, class 1 (1.0 g/m^2) and 3 (0.82 g/m^2) recorded in that year the highest values of the whole time period. However, as suggested in the methodology section of the present study, during 2020 the COVID-19 pandemic could have an impact on the emission factors which will be difficult to quantify.

As will also be the case for aldehydes, both the EU Ecolabel and Italian BAT do not include any threshold for the emission factor of volatile organic compounds, which would be otherwise useful for running a comparison.

3.2.6. *Atmospheric emission of aldehydes*

In **Figure 3-11**, the trend for the emission factor of aldehydes (EF_{Ald}), representative of the Italian ceramic tile sector, is reported over a time span of eleven years.

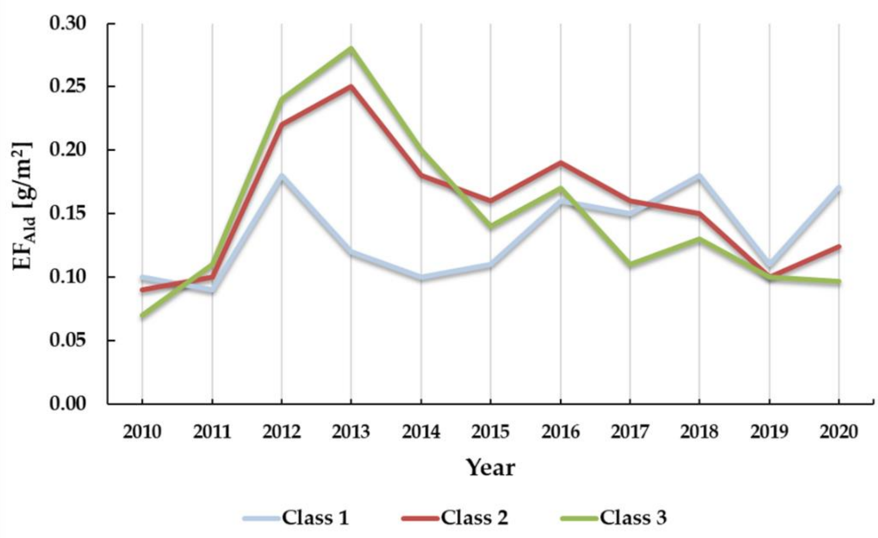


Figure 3-11. Emission factor of aldehydes (EF_{Ald}), represented from year 2010 to 2020, according to the subdivision in the three production classes.

Trends quite resemble the ones just shown for volatile organic compounds for all the three production classes. The emission factors of class 2 and 3, from initial values of 0.09 and 0.07 g/m^2 for class 2 and class 3, respectively, increased until 2013 when reached a maximum value of 0.25 (class 2) and 0.28 g/m^2 (class 3). The trend representing class 1 slightly differs from the others, scoring a maximum of 0.18 mg/m^2 once in 2012 and another time in 2018. However, with the exception of values in 2011, the emission factor of aldehydes registered an important minimum in 2019, equal to 0.11 g/m^2 for class 1 and to 0.10 g/m^2 for class 2 and 3. Then, as shown in the case of volatile organic compounds, values increased again in 2020, during the COVID-19 pandemic.

It is here suggested as the minor number of factories belonging to class 1, as previously reported in **Figure 3-6**, could have contributed to register less consistent values for the emission factors of various pollutants, especially of aldehydes and nitrogen oxides, as it will be soon revealed. It is probably for this reason that the trend representative of class 1 does not adequately resemble the other ones. In fact, this is what should have been expected, being aldehydes, as well as lead and volatile organic compounds, characteristic pollutants related to the firing stage, which is displayed without any substantial difference by all the three production layouts.

3.2.7. Atmospheric emission of nitrogen oxides (NO_x)

In **Figure 3-12**, the trend for the emission factor of nitrogen oxides (EF_{NOx}), representative of the Italian ceramic tile sector, is reported over a time span of eleven years.

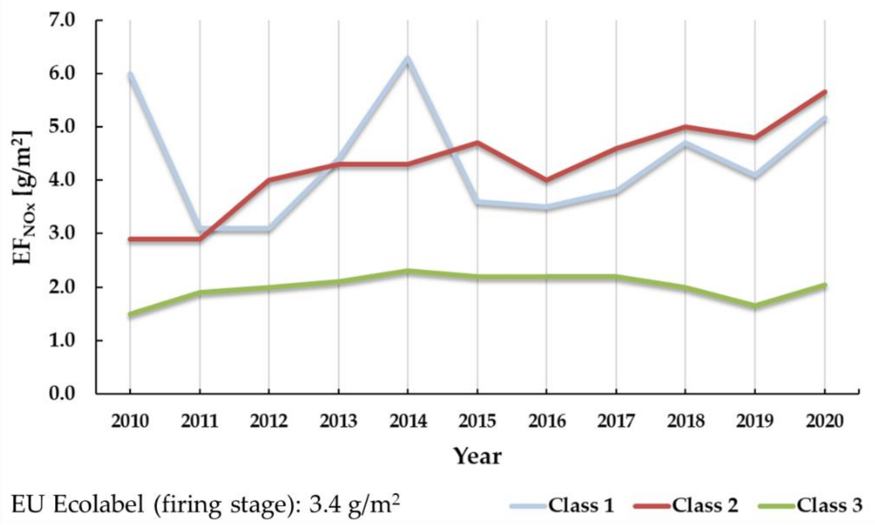


Figure 3-12. Emission factor of nitrogen oxides (EF_{NOx}), represented from year 2010 to 2020, according to the subdivision in the three production classes.

In this case, all the three production classes show a different trend for the emission factor. In particular, it is easy to see that nitrogen oxides emissions for factories belonging to class 1 and 2 has been increasing since 2010, while for class 3 the trend maintained quite constant, ranging from a minimum of 1.5 g/m^2 in 2010, to a maximum of 2.3 g/m^2 in 2014. Even if class 1 quite resemble the constantly increasing trend displayed by class 2, values are far more dispersed. In the years 2010 and 2014, for example, the EF_{NOx} scored quite high values of 6.0 and 6.3 g/m^2, respectively. Class 2, on the other hand started from an initial value of 2.9 g/m^2 and finally counted in 2020 an emission factor equal to 5.7 g/m^2.

The main reason explaining the similarity of trends for class 1 and 2 is that both the mentioned production classes display both the most impacting production stages in terms of nitrogen oxides emissions, namely the spray-drying and firing stage. Factories belonging to class 3, conversely, only feature the firing stage, thus avoiding an important share of emissions related to spray-drying.

Furthermore, with the exception of the reported values for years 2010 and 2014, the trend for class 2 ranks above the one reported for class 1. This fact is easily explained considering the excess of spray-dried powder produced by factories of class 2, a process that does not contribute to the total square meter of product manufactured but actually increases the emission of nitrogen oxides.

The overall increasing trends are then probably to be related to the recent market innovations which favored over the last years an increment in the production of ceramic tiles characterized by higher thicknesses. Simply, the quantity of spray-dried powder necessary for square meter of tiles produced will be higher and higher will be the emissions of nitrogen oxides of the whole manufacturing process. Obviously, this is not the case for factories belonging to class 3, because they purchase the powder, thus evading related emissions.

The EU Ecolabel requires quite a rigorous threshold of 3.4 g/m^2 for the emissions of nitrogen oxides, which regards, however, only the firing stage. The emission factor for Class 3 is under such threshold for the whole time period, while the comparison with the limit cannot be made for classes 1 and 2 as EF_{NOx} considers the sum of emissions comprehensive of both firing and spray-drying stages.

3.2.8. *Atmospheric emission of carbon dioxide (CO_2)*

In **Figure 3-13**, the trend for the emission factor of carbon dioxide (EF_{CO2}), representative of the Italian ceramic tile sector, is reported over a time span of eleven years.

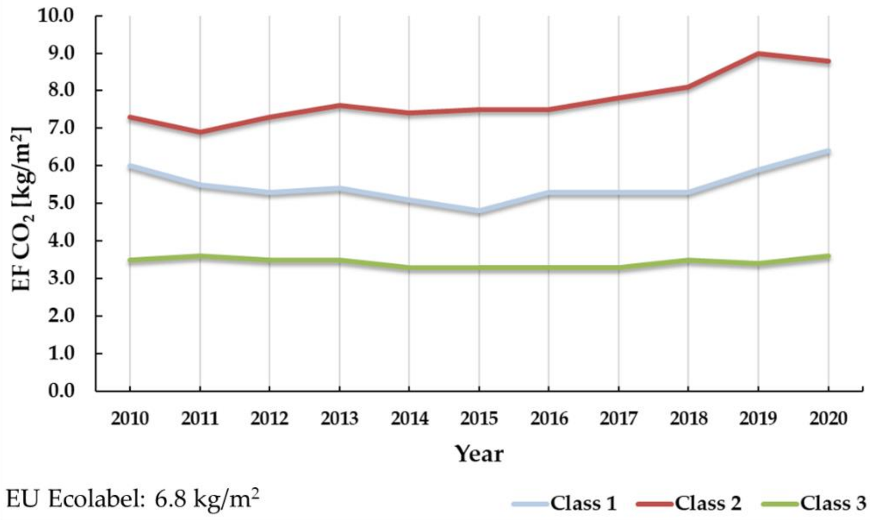


Figure 3-13. Emission factor of carbon dioxide (EF_{CO2}), represented from year 2010 to 2020, according to the subdivision in the three production classes.

Carbon dioxide is the main pollutant linked to high energy involving processes, as it is the case for the whole ceramic industry. This declaration is easily demonstrated by the different unit measure utilized here to describe the emission of carbon dioxide, corresponding to kg/m^2 rather than g or mg/m^2. Also in this case, the amount of released pollutant are totally coherent with the different production layouts. In fact, factories of class 3 exhibit the lowest emission level, mainly because of the lack of one of the most impacting process stage in terms of greenhouse gases emission, that is the spray-drying, besides firing. Values maintained pretty constant all over the time period, scoring around a 3.3-3.6 kg/m^2 range. Conversely, factories belonging to class 2, which conversely display an excess of spray-dried powder, reveal the highest trend of emission, ranging from a minimum of 6.9 kg/m^2 in 2011 to a maximum of 9.0 kg/m^2 in 2019. As expected, class 1 ranks in the middle, with values initially decreasing until 2015, when the lowest emission factor of 4.8 kg/m^2 was registered, and then increasing up to a maximum of 6.4 kg/m^2 in 2020.

Another significant fact that can be noted is the upward progression recorded by classes 1 and 2, in contrast to the steady trend shown by class 3. Such fact could be explained by the increasing thickness of tiles which requires, for the same firing conditions, a greater amount of raw materials and, therefore, a greater use of spray-drying machineries. A similar trend, indeed, is presented in the previous case for the emission of nitrogen oxides, which are gasses strictly related to this stage of the production process. This explanation could account for the trends reported in the two cases, although it remains purely a hypothesis and the pollutant trends would have to be related to the specific production of the plants to confirm this interpretation.

The EU Ecolabel sets 6.8 kg/m^2 as the threshold for environmental excellence, calculated for the sum of the spray-drying and firing process. Thus, according to the reported data, the annual emission factor for factories belonging to both class 1 and 3 has been under the excellence limit for the whole time period. On the other hand, class 2 always provided higher emission factors, even if a portion of these emissions is actually corresponding to the amount spared by those factories which do not display the ceramic body preparation step and, thus, do not present spray-drying facilities inside them.

3.2.9. Conclusions

In the present study, the trend of the emission factors of the most characteristic pollutants of the ceramic tile industry have been reported over a time period greater than eleven years and commented accordingly. The data reported here, and the related discussion helped in describing and interpreting the environmental impact in terms of atmospheric emissions of the Italian ceramic tile sector.

Particularly, the following evidence can be drawn:

- The emission factors of particulate matter, fluorine and lead compounds continuously decreased over the last two decades, stabilizing to very low values compared to the best available techniques as stated in the D. M. of 29 January 2007 and to EU Ecolabel requirements. The advances in the technological innovation of manufacturing processes demonstrated by ceramic tile factories has certainly contributed to achieve such optimal results. Furthermore, the introduction through revisions of the IPPC directive and the consequent intensification and improvement of atmospheric monitoring have also certainly helped to keep atmospheric emissions monitored.
- The emission factors of volatile organic compounds, aldehydes and nitrogen oxides has been increasing over the considered time period. This fact is probably related to the technologies required to satisfy the current market's requests. In particular, it was presented as the merger of ink decorations has led to a substantial increase in the emission of VOCs and aldehydes. It was also referred as the increased thickness of tiles could have led to an increment in the emission of nitrogen oxides. It is here suggested as the marketing of more sustainable practices and technologies can be used to push consumers to also award the sustainability of the production processes rather than only the aesthetic or quality of final products.
- There is a strong necessity to harmonize all the different environmental regulations and quality standard in terms of unit of measure of the performance indicators. Limits are differently represented in g/m^{2,} or g/kg of tiles manufactured, in mg/Nm^3 of air flow and even in kg/year of pollutant emitted (Commission Decision (EU) 2021/476 of 16 March 2021; *D. M. 29 Gennaio 2007; European Industrial Emissions Portal*). A standardization in the regulations language is fundamental for an effective interpretation of data and for a better understanding of the strengths and weaknesses exhibited by the Italian ceramic tile sector.

The data represented and the results obtained demonstrate how the technological innovations adopted over the years and the increased attention to pollutant containment have contributed to the improvement of air quality in the Sassuolo ceramic district, taken as representative of the entire Italian ceramic tile production. However, there is further room for improvement, and the revision of the national regulation and the pursuit for the current best available techniques can help to address such goals.

In addition, it was revealed as the market requirements can easily influence and dictate the emission of certain pollutants. Thereby, it is suggested as the marketing can play a fundamental role in the sustainable transition of the ceramic tile sector in Italy by encouraging consumers to invest in the quality of Italian products and to award sustainability as an essential aspect of quality.

3.3. Data collection on current legal limits and actual emissions positioning of the ceramic tile industry

Another important activity carried out during this research project has been the determination of the positioning of actual emission performance of Italian ceramic tile factories with respect to current legal limits enacting at international and national level. In fact, at the light of the discussion on the revision of the CER BREF document, it is important to define actual emission trends and spot weaknesses of the current scheme to better perceive the direction to follow when bringing new or stricter limits on the discussion board.

A vast data collection has been devised in order to gather data from 57 Italian ceramic tile producers of the Emilia-Romagna region concerning permitted limits and registered emissions for the year 2018. Data regarding the concentration of some main pollutants of the production process of ceramic tiles have been compared to maximum and minimum limits among environmental authorizations, yielding a photography of the actual environmental performance among factories of the sample. The discussion have been focusing on three most impacting processes in terms of environmental pollution and health and safety of working environments, namely spray-drying, pressing and firing stages. No distinction was made between production layouts because the concentration data for each pollutant, in this case, refer to each individual emission point and are not strictly representative of the production cycle. As mentioned, differentiation was made according to the specific productive step.

Thus, it was possible to identify the high variability of data, especially those regarding the legal limits as stated by the specific AIA document for each industrial installation, and to make a comparison with the international regulation, here represented by the CER BREF document. Indeed, it is here recalled how an AIA document, unique for each industrial plant, may require a specific emission limit and add additional monitoring actions based on the peculiar environmental situation of the area where the ceramic factory is located. This explains the high variability of emission limits in force among Italian ceramic tile manufacturers.

The present assessment has demonstrated how the Italian ceramic tile sector can stand as an example of commitment to sustainability and technological innovation among industrial realities, by virtue of the optimal proven environmental performance which effectively adhere to best available techniques and international requirements at European level.

3.3.1. Methodology of data collection and analysis

Data have been collected on the public web portal of ARPAE (*Homepage - Autorizzazione Integrata Ambientale - Regione Emilia Romagna*) referring to 57 producers of ceramic tiles, mainly represented by porcelain stoneware, located in the Emilia-Romagna region, according to the distribution in provinces represented in **Figure 3-14**.

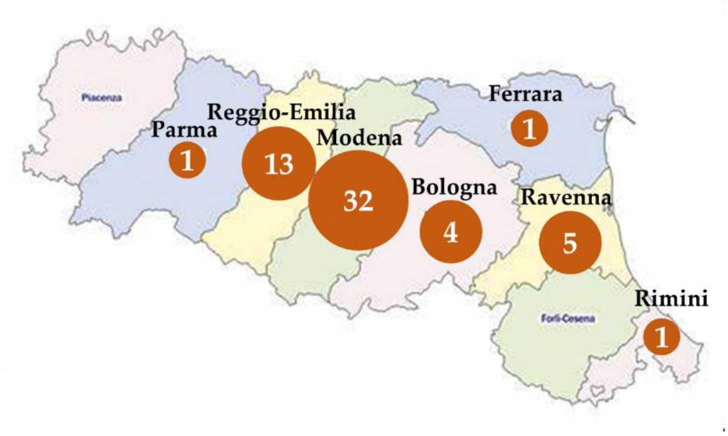


Figure 3-14. Number of ceramic tile factory of the sample distributed in the Emilia-Romagna region, according to sub-distribution in provinces.

Permitted limits and measured values have been defined as follows:

- Limits: these are the permitted limits of concentration for each pollutant as stated by the specific AIA document for each industrial installation. Data are expressed in mg/Nm^3. Emission ranges from the ceramic BREF, instead, are reported in mg/m^3, as listed inside the mentioned document.
- Measured values: these are the values of the singular measured concentration for each pollutant furnished by each factory and related to year 2018, as reported in the environmental reports available on the web portal of ARPAE (*Homepage - Autorizzazione Integrata Ambientale - Regione Emilia Romagna*), of public domain, in compliance with Industrial Emission Directive of the European Union. All data are expressed in mg/Nm^3, that is all the measures were standardized to 0 °C of temperature and 1 atm of pressure.

  Data related to the spray-drying stage are expressed considering the environmental concentration of oxygen equal to 17.5%, chosen as representative value for the atmosphere inside the spray-dryer equipment.

Data related to the firing stage are expressed considering the environmental concentration of oxygen equal to 16.5%, chosen as representative value for the atmosphere inside kilns.

The recalculation of data that, at the time of sampling, were not coherent with the reference oxygen conditions was performed by using a correction factor for oxygen obtained according to the following equation:

$$Correction\ factor\ O_2 = \frac{(21 - reference\ O_2)}{(21 - measured O_2)}$$

All permitted limits were divided into categories according to most occurring threshold values. The different categories were depicted by colors, from the strictest limit, in green, to the most tolerant one, in red.

All measured values were expressed as maximum, minimum, mean and median values. Then, data for each pollutant were reported in graphs for visualization purposes and compared to the mean values and with the maximum and minimum limits found in the AIA documents. When available, the value expressed in the CER BREF was also reported in order to make a comparison between the national performance and the emission levels associated to the best available techniques (BAT-AELs).

The sampling methods of all the pollutants considered in the present section were accessed from the AIA documents and were the same listed in **section 3.2.1**.

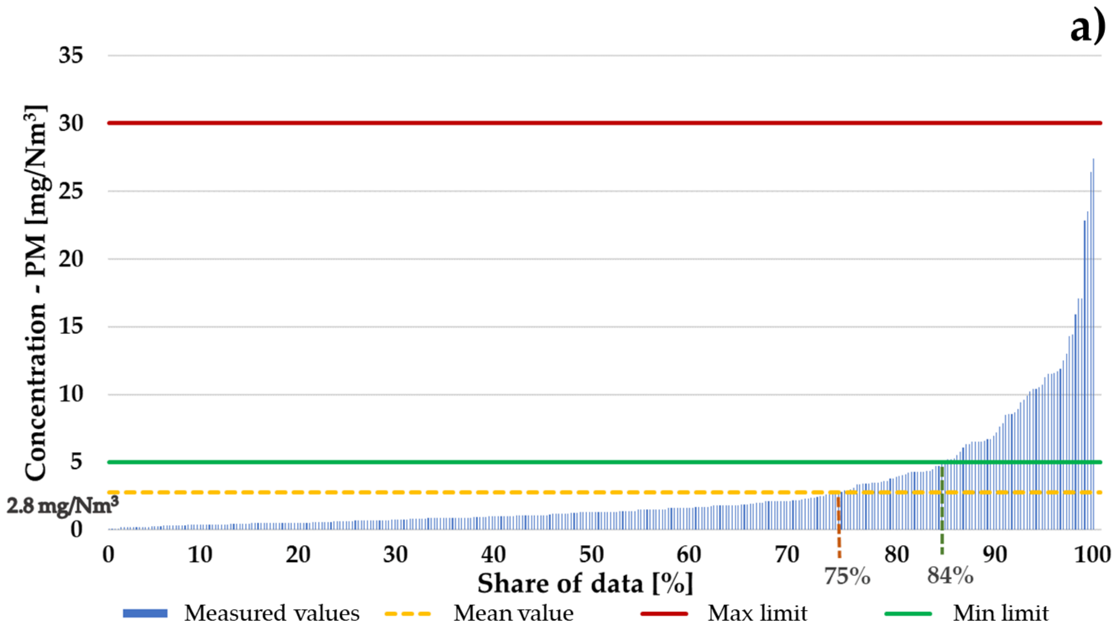
3.3.2. Spray-drying stage – Limits and emission values

The pollutant treated in the section dedicated to the spray-drying stage are the particulate matter (PM) and the nitrogen oxides (NO_x), which are the characteristic pollutants associated with the spray-dryer equipment. In fact, as previously described, this stage is characterized by a particular level of dustiness, because of the involvement of fine milled raw materials, while partial oxidized species of nitrogen are formed during the combustion of natural gas or carried by the hot streams of exhausted air coming from cogeneration plants.

Other pollutants, as fluorine compounds and sulfur oxides are not characteristic of this production stage because the temperature involved in the spray-drying process (around 500 °C) are not high enough to cause the collapse of the clay structure and consequently release these chemical species. Likewise, lead oxide and volatile organic species are pollutants which are related to pigments and glaze formulations and, thus, cannot be found in all those processes ahead of the decoration stage.

3.3.2.1. Spray-drying stage – Particulate matter

In **Figure 3-15 a)** and **b)** are reported the measured concentration values for the particulate matter related to the spray-drying process, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. All the permitted limits were collected and divided in categories according to most occurring ranges, as represented in **Figure 3-15 c)**.



b)

Measured values - PM (17,5% O$_2$)			
N° measures	Max value	Min value	Median
326	27,4 mg/Nm^3	0.09 mg/Nm^3	1.3 mg/Nm^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
1-30 mg/Nm^3	30 mg/Nm^3	5 mg/Nm^3	20 mg/Nm^3

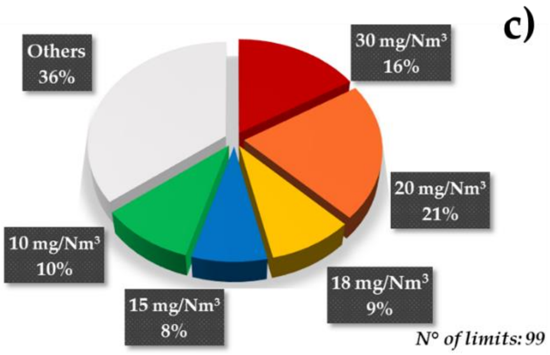


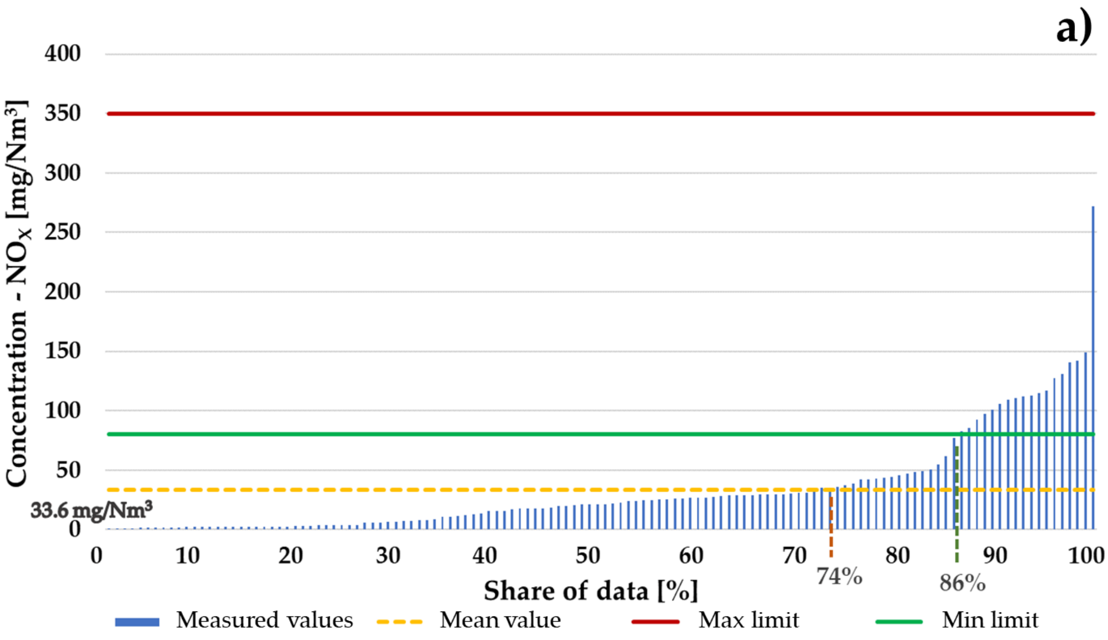
Figure 3-15. a) Measured concentrations values of particulate matter (PM) for the spray-drying stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

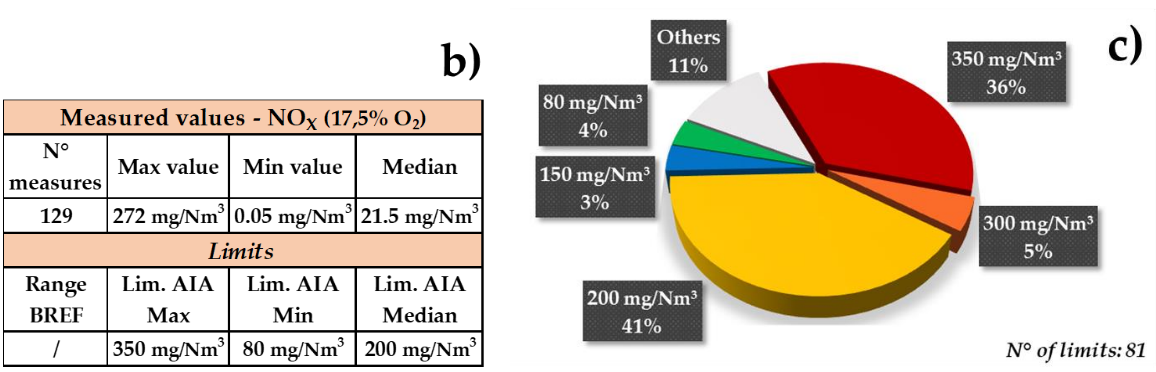
Among the 326 collected measures of particulate matter, 84% of them are under the strictest limit found in the among the AIA documents, equal to 5 mg/Nm^3. Notably, the highest limit of 30 mg/Nm^3, which is also presented as the threshold values associated with the BATs, is never exceeded. Furthermore, 75% of all the measures is under the average, suggesting that high concentration values are less probably encountered compared to lower ones, observation being also confirmed by the fact that the median (1.3 mg/Nm^3) is lower than half of the mean (2.8 mg/Nm^3). However, the rightest portion of the data in **Figure 3-15 a)** indicates how to spray-dryer machineries can still be associated high concentrations of particulate matter, being values above 10 mg/m^3 sign of a particularly dusty process.

On the other hand, the ranges of permitted limits illustrated in **Figure 3-15 c)** show a notable variability of the sample, especially expressed by the high share (36%) of limits not frequently encountered. This fact could be associated to the different environmental situations for each ceramic tile factory or to the particular spray-dryer and abatement technologies that have been customized over the years.

3.3.2.2. Spray-drying stage – Nitrogen oxides

In **Figure 3-16 a)** and **b)** are reported the measured concentration values for the nitrogen oxides associated to the spray-drying process, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. All the permitted limits are divided in categories according to most occurring ranges, as represented in **Figure 3-16 c)**. Also in this case, data are expressed considering the environmental concentration of oxygen equal to 17.5%.





b)

Measured values - NO_X (17,5% O_2)			
N° measures	Max value	Min value	Median
129	272 mg/Nm^3	0.05 mg/Nm^3	21.5 mg/Nm^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
/	350 mg/Nm^3	80 mg/Nm^3	200 mg/Nm^3

Figure 3-16. a) Measured concentrations values of nitrogen oxides (NO_X) for the spray-drying stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

Compared to the case of particulate matter, for nitrogen oxides there is a lower number (126 values) of measures in the sample. However, trends are very similar. In fact, 86% of the concentration values are under the minimum limit of 80 mg/Nm^3, while 74% of them are under the mean. Also in this case, the median (21.5 mg/Nm^3) is lower than the mean (33.6 mg/Nm^3), indicating a greater presence of low concentration measures. Interestingly, with the exception of only one quite high value, the entirety of the measures stands well below the maximum permitted limit (350 mg/Nm^3), more in particular below 150 mg/m^3.

It is also interesting to note that, in comparison to particulate matter, values of concentration for nitrogen oxides are one order of magnitude higher. Thus, even if particulate matter is instinctively perceived as a threat, invisible gaseous pollutants as nitrogen oxides, can actually be emitted to far greater amount without the human perception.

The ranges of permitted limits illustrated in **Figure 3-16 c)** suggest that, probably, the once common limit of 350 mg/Nm^3 is progressively being amended with a stricter cap of 200 mg/Nm^3, because of the high number of such values. Other limits, on the other hand, are presumably to be ascribed to peculiar environmental situation of certain factories which have led to more rigid environmental authorizations.

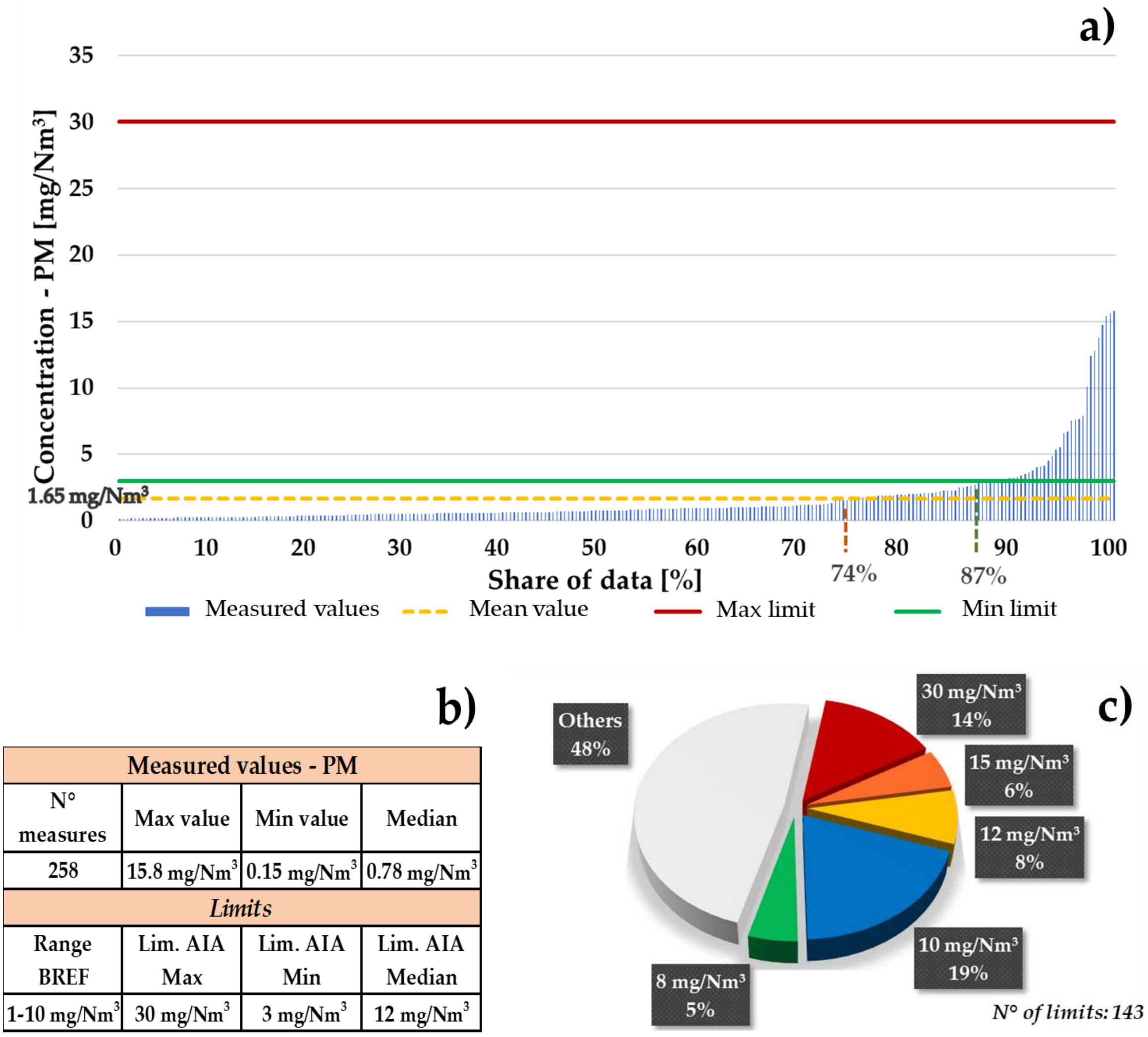
3.3.3. *Pressing stage – Limits and emission values*

After spray-drying, the pressing stage is the second responsible of the highest levels of dustiness within ceramic tile factories. The consolidation process of spray-dried granules, in fact, can release particulate matter up to great amounts, especially when the humidity of granules has not been perfectly regulated.

No other pollutants are related to this stage.

3.3.3.1. Pressing stage – Particulate matter

In **Figure 3-17 a)** and **b)** are reported the measured concentration values for the particulate matter associated to the pressing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. In **Figure 3-17 c)** all the permitted limits are divided in categories according to most occurring ranges.



Measured values - PM			
N° measures	Max value	Min value	Median
258	15.8 mg/Nm^3	0.15 mg/Nm^3	0.78 mg/Nm^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
1-10 mg/Nm^3	30 mg/Nm^3	3 mg/Nm^3	12 mg/Nm^3

Figure 3-17. a) Measured concentrations values of particulate matter (PM) for the pressing stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

Similar to the previous cases, the percentages of concentration values standing under the mean (74%) and the strictest permitted limit (87%) are quite high. The highest limit (30 mg/Nm^3), moreover, is never exceeded and almost all of the 258 measures are under the half of it.

As it happen for the spray-drying stage, **Figure 3-17 c)** shows a high variability in the sample of permitted limits, which is actually quite abundant, counting 143 values. An important share is represented by a cap of 10 mg/Nm^3 but the 48% of the environmental authorizations demand particular limits, probably due to the changes in the number of pressing machineries during the years inside the same factory. In fact, when a new plant is added to the manufacturing process and consequently included in the AIA document, the cap for the emissions allocated for the same process can be split between plants or altered according to the modifications carried out on the equipment.

However, it shall be noted as the best available techniques suggest an associated emission value equal to 10 at the most, as indicated by the BREF range. Therefore, all higher limits could refer to special environmental backgrounds or be ascribed to old AIA that still need to be renovated.

3.3.4. *Firing stage – Limits and emission values*

Because of the great fuel consumption and the high temperatures involved during firing, kilns are indubitably the most environmentally impacting equipment of the whole production process of ceramic tiles.

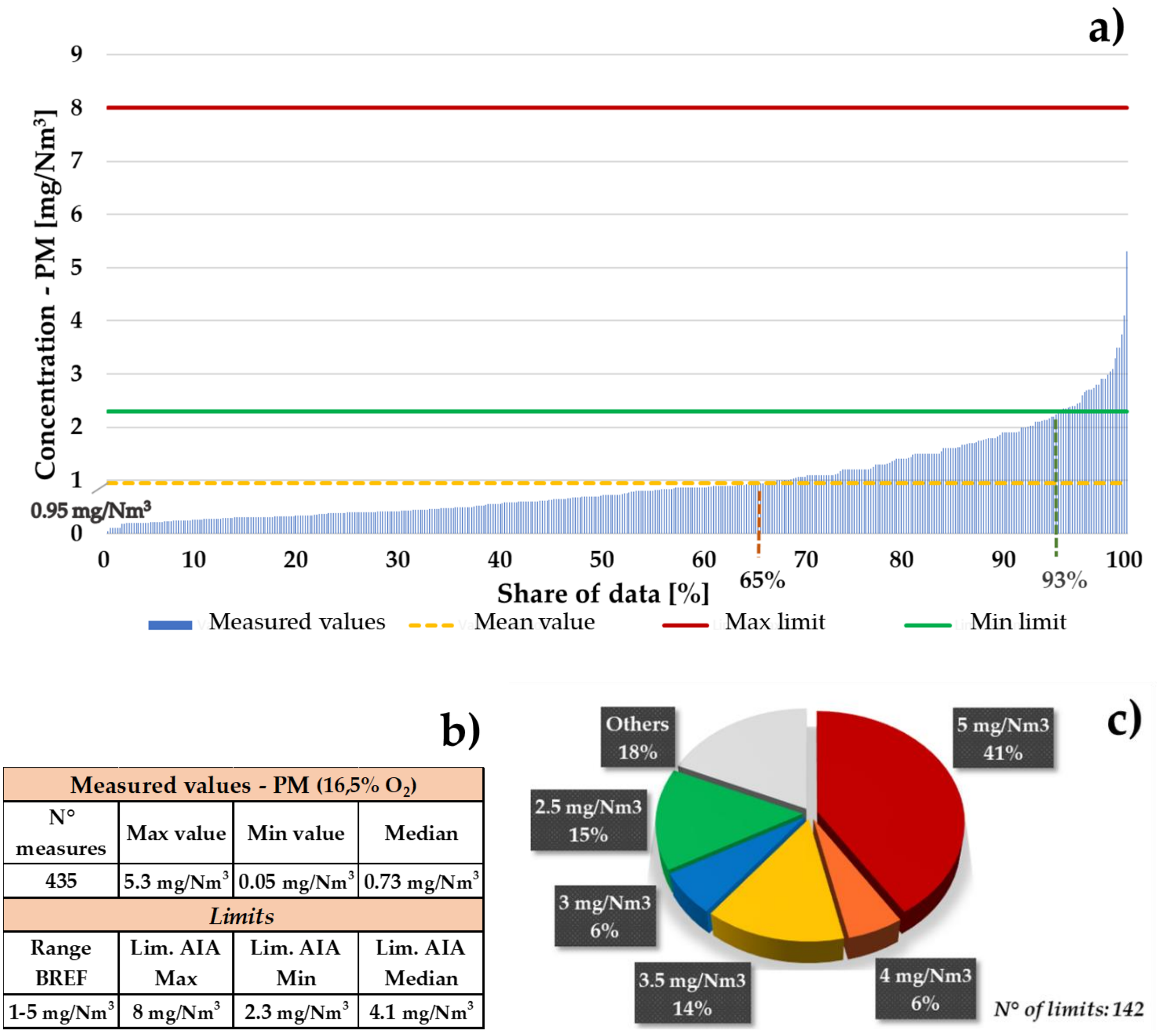
Thanks to the sintering of the ceramic body, quite low concentration levels of particulate matter are associated to the firing stage. However, other pollutants are characteristic of the process, as fluorine compounds and nitrogen (NO_x) and sulfur oxides (SO_x), while others, even if not properly distinctive of firing operations but rather of decoration procedures, as lead (Pb) and volatile organic compounds (VOCs), are released inside kilns as a consequence of chemical reactions.

In this chapter, aldehydes were treated as a separated class of pollutants, even though are actually volatile organic compounds. In fact, when reporting data for VOCs, the concentration values will be comprehensive also for the portion of aldehydes, which must be though accounted separately according to most of the environmental authorizations. Some of the representatives of this class of chemical compounds that can be encountered inside flue gasses from the firing process are formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and benzaldehyde.

Notwithstanding the improvements in the sustainability of the whole production process, it shall be highlighted that the continuous progress in the ceramic technology and in industrial engineering is the key factor for a further reduction in the emissions of pollutants, or for their complete eradication as, for example, in the case of lead (Pb). In this regard, working on reducing the impact of the firing stage can radically change the environmental footprint of this whole industrial sector.

3.3.4.1. Firing stage – Particulate matter

In **Figure 3-18 a)** and **b)** are reported the measured concentration values for the particulate matter associated to the firing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. **Figure 3-18 c)** reports all the permitted limits divided in categories according to most occurring ranges.



Measured values - PM (16,5% O_2)			
N° measures	Max value	Min value	Median
435	5.3 mg/Nm³	0.05 mg/Nm³	0.73 mg/Nm³
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
1-5 mg/Nm³	8 mg/Nm³	2.3 mg/Nm³	4.1 mg/Nm³

Figure 3-18. a) Measured concentrations values of particulate matter (PM) for the firing stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

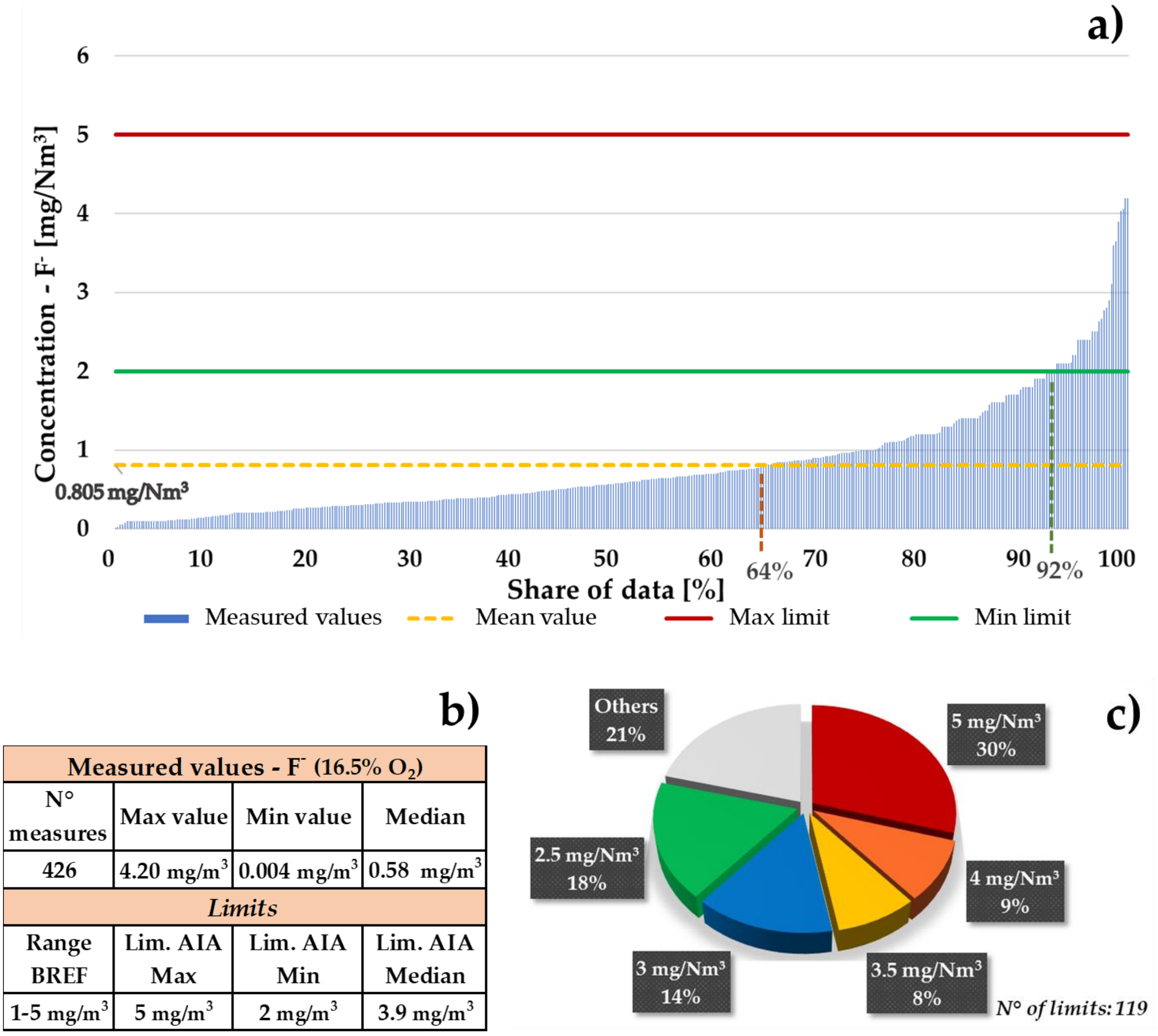
The number of measures (435 values) reported in **Figure 3-18 a)** is the highest among the cases treated in this chapter. 93% of them stands under the strictest permitted limit, equal to 2.3 mg/Nm³, while 65% ranked inferior to the average value of 0.95 mg/Nm³. Only one value exceeds the maximum of the BAT-AEL of 5 mg/m³, which is also the most common permitted limit (41% of share, as illustrated in **Figure 3-18 c)** among all

142 values extracted from the AIA documents. The maximum permitted limit of 8 mg/Nm^3 is probably related to a peculiar environmental situation and, in fact, is not generally authorized.

Data suggest that the environmental performance related to the firing process in the case of particulate matter is perfectly in line with the emission levels predicted by the best available techniques presented inside the ceramic BREF.

3.3.4.2. Firing stage – Fluorine compounds

In **Figure 3-19 a)** and **b)** are reported the measured concentration values for the particulate matter associated to the pressing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. In **Figure 3-19 c)** all the permitted limits are divided in categories according to most occurring ranges.



Measured values - F$^-$ (16.5% O_2)			
N° measures	Max value	Min value	Median
426	4.20 mg/m^3	0.004 mg/m^3	0.58 mg/m^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
1-5 mg/m^3	5 mg/m^3	2 mg/m^3	3.9 mg/m^3

Figure 3-19. a) Measured concentrations values of fluorine (F$^-$) for the firing stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean

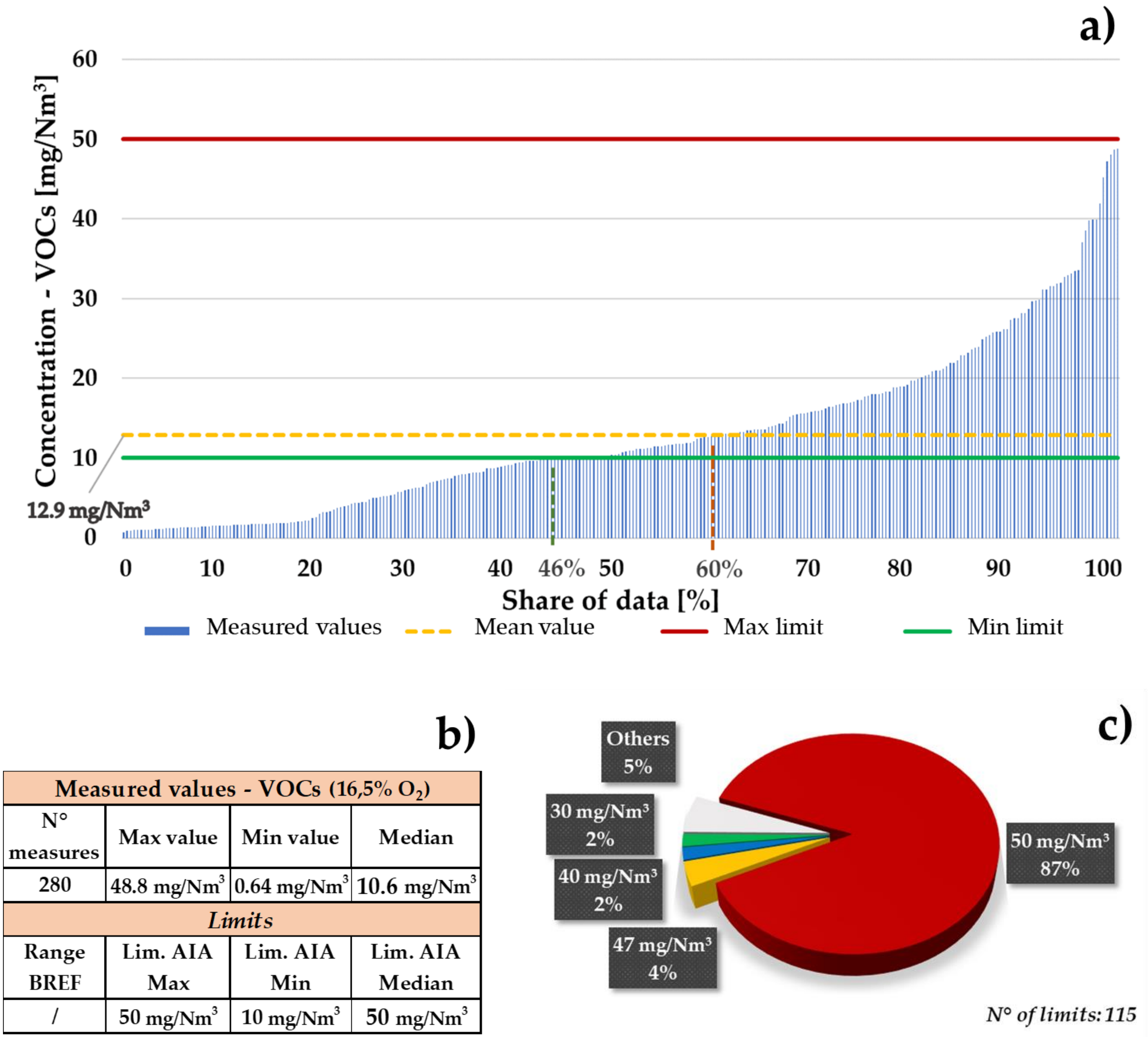
values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

Also in this case, the number of measures (426 values) is quite important. The strictest among the permitted limits found in the AIA documents, equal to 2 mg/Nm^3, is exceeded by only 8% of all values. The mean concentration of 0.805 mg/Nm^3 and the median of 0.58 mg/Nm^3 testify that fluorine compounds, here expressed as fluoride ion, are successfully retain by the filtering devices. In fact, even if the highest limit of 5 mg/Nm^3 is represented by the highest share (30%) among categories in **Figure 3-19** c), and it is also the cap proposed in the ceramic BREF, almost the entirety of the values in the sample is far lower than such limit. Other categories can be the result of stricter authorizations as a consequence of particular environmental backgrounds. On the other hand, the limit of 2.5 mg/Nm^3 could also be related to the introduction of an additional kiln in the same installation without further emissions of fluorine being conceded by the amended AIA, fact that could have been led to the splitting of the highest limit.

Finally, it shall be noted as the exponential-alike trend of values increasing in the right part of the graph in **Figure 3-19 a)** can be a hint of the fact that, if not efficiently contained, fluorine emission can easily get out of control and increase rapidly beyond the even most tolerant limit.

3.3.4.3. Firing stage – Volatile organic compounds (VOCs)

In **Figure 3-20 a)** and **b)** are reported the measured concentration values for volatile organic compounds (VOCs) associated to the firing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. **Figure 3-20 c)** reports all the permitted limits divided in categories according to most occurring ranges.



Measured values - VOCs (16,5% O_2)			
N° measures	Max value	Min value	Median
280	48.8 mg/Nm^3	0.64 mg/Nm^3	10.6 mg/Nm^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
/	50 mg/Nm^3	10 mg/Nm^3	50 mg/Nm^3

Figure 3-20. a) Measured concentrations values of volatile organic compounds (VOCs) for the firing stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

Differently from the previous cases, data concerning the emissions of volatile organic compounds, counting 280 measures, are quite more distributed to higher concentration values. However, it shall be highlighted as only few values are near the highest permitted limit of 50 mg/Nm^3, which is also the most represented among limit categories, with an 87% share.

This can be related to the fact that volatile organic compounds are a rather new pollutant of the production process of ceramic tiles. In fact, these chemical species are mostly released inside kilns after the vaporization and pyrolysis of organic additives or the organic media in which the ceramic pigments for ink-jet decoration are suspended. Being such technology quite new to the ceramic industry, the containment practice of this class of pollutants have not yet been refined and tuned to an optimal standard. The fact that there is no threshold concentration range set by the ceramic

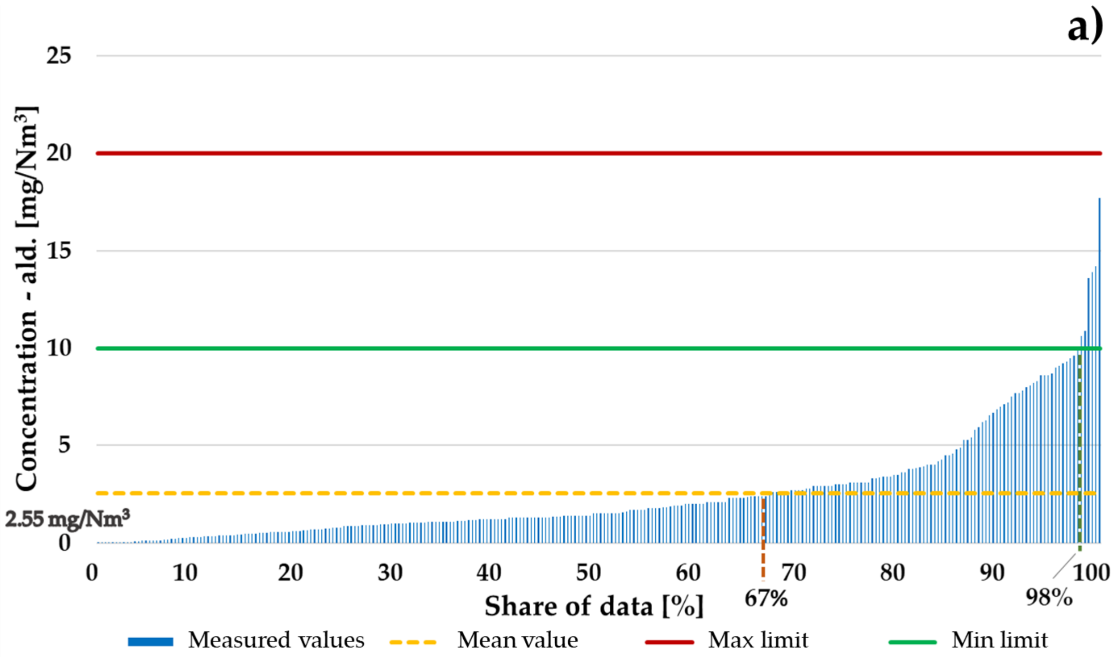
BREF supports this interpretation. Nonetheless, as exposed in **section 2.6**, the Italian decree D. M. of 29 January 2007 reports threshold values for both VOCs and aldehydes, suggesting how Italy was paying in this case particular attention to an issue that at the beginning was probably not internationally perceived (*D. M. 29 Gennaio 2007*).

Actually, volatile organic compounds can also be released after the burning of the organic matter that is carried in little amounts by clays. However, as it was illustrated in **section 3.2.5**, the concentration of these pollutants at the emissions of ceramic tile factories has been growing over the last decades in conjunction with the increasing introduction of digital ink-jet decoration techniques.

Nonetheless, 46% of the data stands under the minimum permitted limit of 10 mg/Nm^3 while a 60% under the mean value of 12.9 mg/Nm^3. Furthermore, the closeness between this latter value and the median (10.6 mg/Nm^3) suggests that the distribution is quite symmetrical and there is a similar probability to collect very high as very low values.

3.3.4.4. Firing stage – Aldehydes

In **Figure 3-21 a)** and **b)** are reported the measured concentration values for aldehydes associated to the firing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. In **Figure 3-21 c)** all the permitted limits are divided in categories according to most occurring ranges.



b)

Measured values - Aldehydes (16,5% O_2)			
N° measures	Max value	Min value	Median
274	17.7 mg/Nm^3	0.02 mg/Nm^3	1.5 mg/Nm^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
/	20 mg/Nm^3	10 mg/Nm^3	20 mg/Nm^3

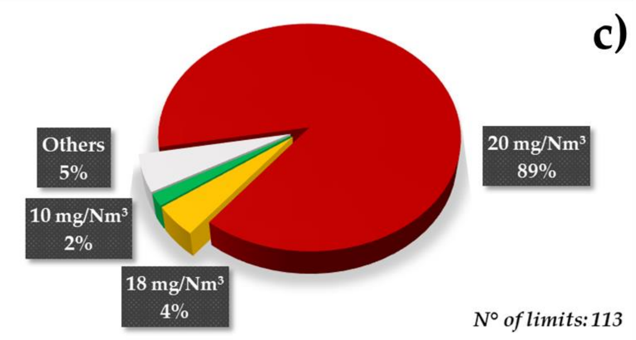


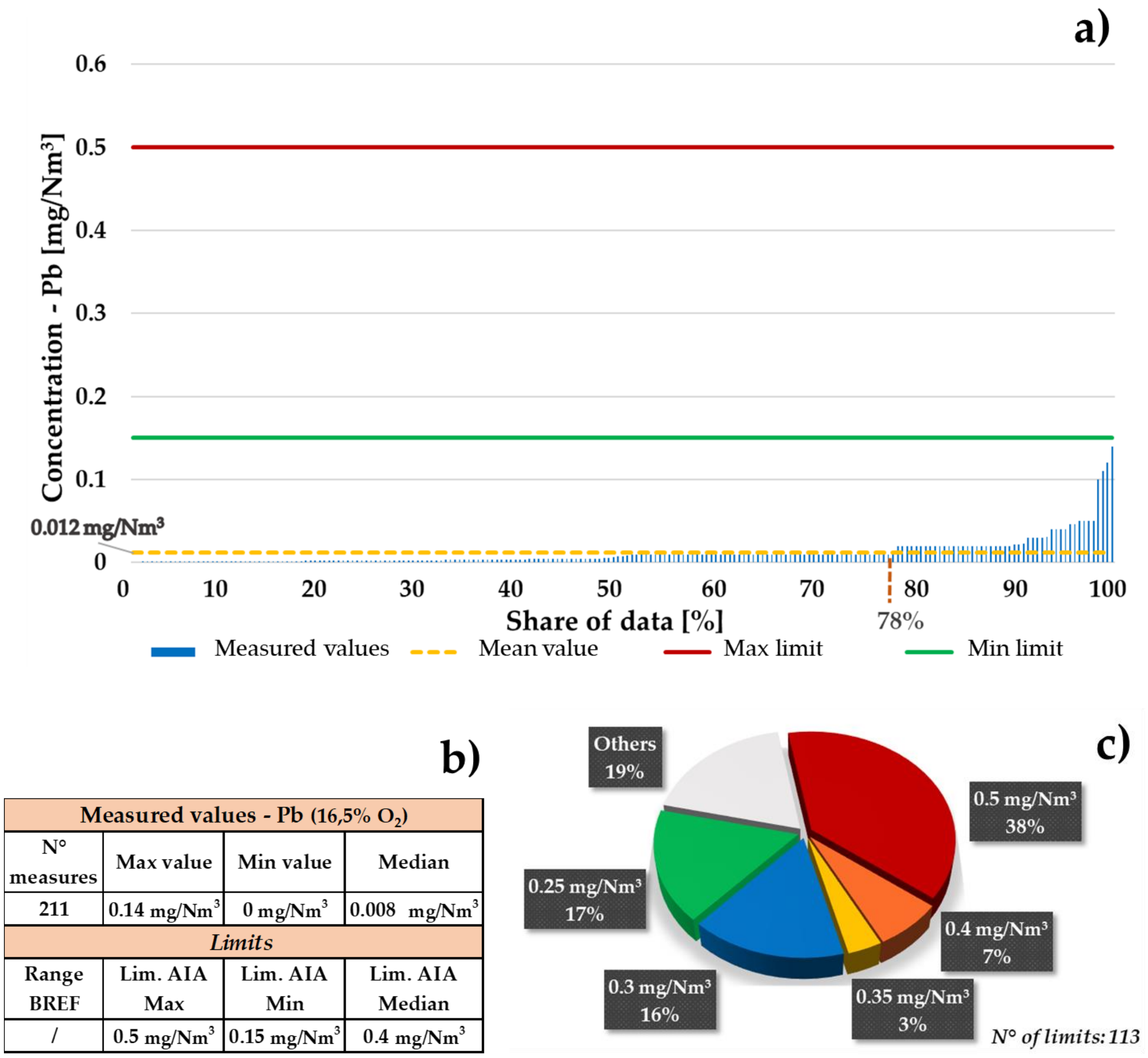
Figure 3-21. a) Measured concentrations values of aldehydes for the firing stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

It is easy noticed that number of measures for aldehydes (274 values) is similar to those collected for volatile organic compounds (280 values). In fact, as previously mentioned, aldehydes are actually volatile organic molecules characterized by low molecular weight that can remain in the atmosphere for quite a long time after their release. Thus, whenever an environmental authorization require the quantification of VOCs, in almost all cases the characterization of the aldehydes' fraction will be compelling. Indeed, aldehydes are particularly reactive chemical species and can manifest a serious hazard to human health, some of them accounted for potential carcinogenic concern, as formaldehyde and acetaldehyde (O'Brien, Siraki and Shangari, 2005).

The trend of data, however, is rather different if compared to that of volatile organic compounds, illustrated in the previous case. The 67% of all measures stands under the mean value of 2.55 mg/Nm^3, while 98% of these comply with the strictest limit of 10 mg/Nm^3, even if being representative of only the 2% of the 113 limits found inside the AIA documents. Indeed, the most occurring permitted limit is of 20 mg/Nm^3, with a 89% share of representation.

3.3.4.5. Firing stage – Lead (Pb)

In **Figure 3-22 a)** and **b)** are reported the measured concentration values for the lead compounds (Pb) associated to the firing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. **Figure 3-22 c)** reports all the permitted limits divided in categories according to most occurring ranges.



b)

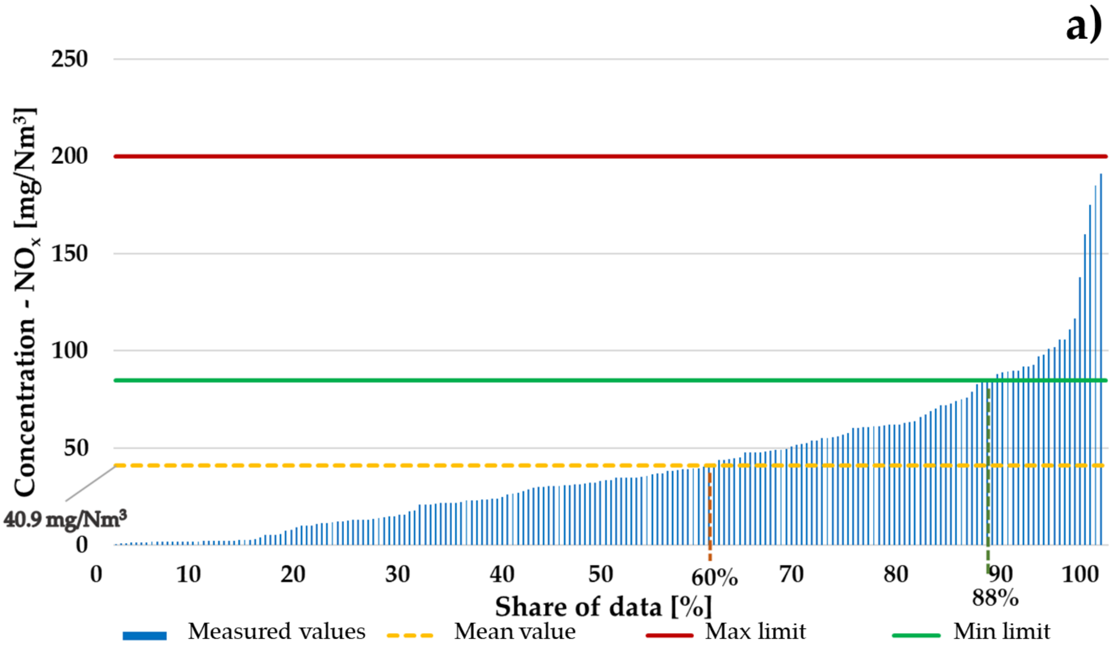
Measured values - Pb (16,5% O_2)			
N° measures	Max value	Min value	Median
211	0.14 mg/Nm³	0 mg/Nm³	0.008 mg/Nm³
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
/	0.5 mg/Nm³	0.15 mg/Nm³	0.4 mg/Nm³

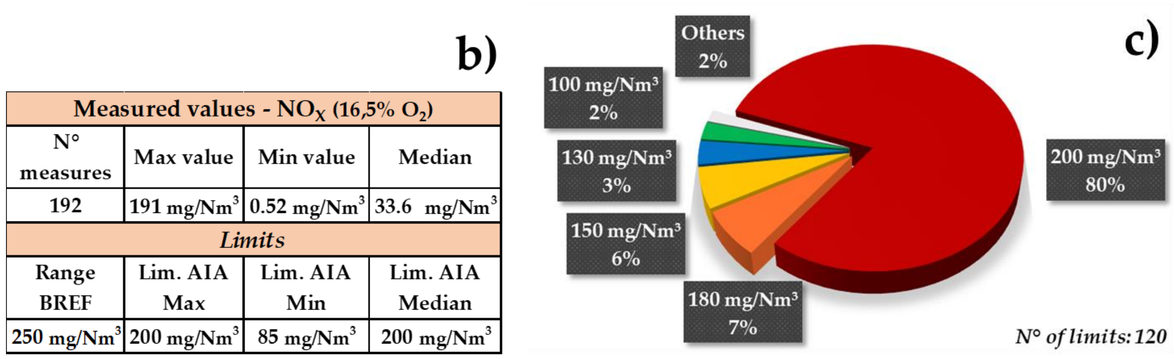
Figure 3-22. a) Measured concentrations values of lead (Pb) for the firing stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

Once a characteristic ingredient of ceramic pigments and glazes, because of the capacity to impart a peculiar gloss to ceramic surfaces, lead has almost entirely been substituted by the use of less toxic elements. As a consequence, lead compounds are hardly found at the emissions of ceramic tile factory and this pollutant has almost been eradicated from the production processes. This statement is easily supported by the data in **Figure 3-22 a)**. In fact, among 211 measures, only three exceed 0.1 mg/Nm³, which is still a threshold five times lower than the highest and most frequently occurring permitted limit of 0.5 mg/Nm³ found inside the AIA documents. In addition, even if the mean value is 0.012 mg/Nm³, probably most of the concentration measures reported under such value are in fact equivalent with the limit of quantification (LOQ) of the different methods of analysis through which the concentration of lead has been calculated. Actually, a concentration of 0 mg/Nm³, reported as the minimum value among data, is not scientifically reasonable. However, it was decided to present the data faithfully according to the environmental reports provided by the companies. Furthermore, the ceramic BREF does not offer any threshold limit for lead compounds. This fact suggests that the future direction will be to eliminate the requirements for the quantification of such pollutants also from the environmental authorizations emitted in Italy by the regional bureaus for environmental protection.

3.3.4.6. Firing stage – Nitrogen oxides (NO_x)

In **Figure 3-23 a)** and **b)** are reported the measured concentration values for nitrogen oxides (NO_x) associated to the firing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. In **Figure 3-23 c)** all the permitted limits are divided in categories according to most occurring ranges.





Measured values - NO_X (16,5% O_2)			
N° measures	Max value	Min value	Median
192	191 mg/Nm^3	0.52 mg/Nm^3	33.6 mg/Nm^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
250 mg/Nm^3	200 mg/Nm^3	85 mg/Nm^3	200 mg/Nm^3

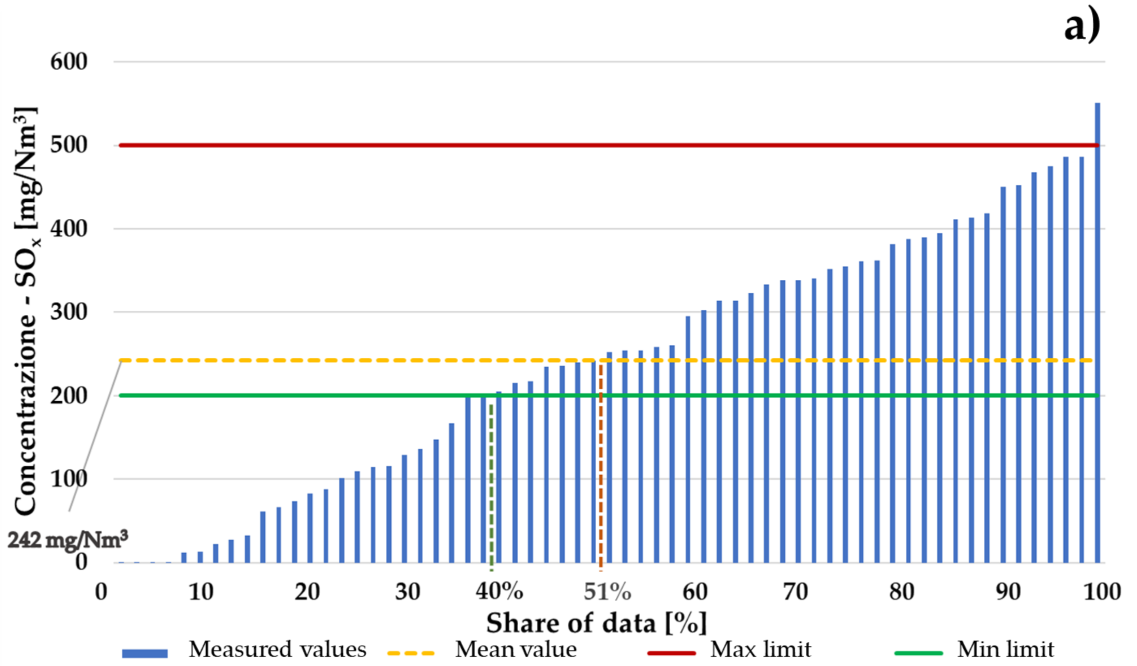
Figure 3-23. a) Measured concentrations values of nitrogen oxides (NO_x) for the firing stage, compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

Similar to the case of VOCs and aldehydes, also for nitrogen oxides there are few different limit categories, as illustrated in **Figure 3-23 c)**. Among 120 values, an 80% share is represented by the highest limit of 200 mg/Nm^3 which, interestingly, is lower than the emission threshold suggested by the ceramic BREF. However, the 88% of all concentration measures stands below the most rigorous limit found inside the AIA documents, equal to 80 mg/Nm^3. Even so, such limit is actually enforced by less than 2% of industrial installations. In addition, 60% of all values ranks under the mean of 40.9 mg/Nm^3.

With the exception of the rightest portion of the trend, the data exposed in **Figure 3-23 a)** display a constant increasing progression from 0.52 mg/Nm^3 up to higher concentrations, suggesting as nitrogen oxides are pollutants which presence can hardly be restrained. These chemical species, in fact, are the result of a whole series of side reactions occurring during the combustion of natural gas, which would ideally produce only water vapor and carbon dioxide as by products. However, even if the currently adopted fuels would be replaced by more green alternatives, as hydrogen, to achieve sintering inside ceramic kilns, the actual combustion process will always generate a quantity of nitrogen oxides different from zero.

3.3.4.7. Firing stage – Sulfur oxides (SO_x)

In **Figure 3-24 a)** and **b)** are reported the measured concentration values for the sulfur oxides (SO_x) associated to the firing stage, together with the maximum and minimum limits found inside the environmental authorizations, *i.e.*, AIA documents. **Figure 3-24 c)** reports all the permitted limits divided in categories according to most occurring ranges.



b)

Measured values - SO_X (16,5% O_2)			
N° measures	Max value	Min value	Median
62	550.7 mg/Nm^3	1.1 mg/Nm^3	247 mg/Nm^3
Limits			
Range BREF	Lim. AIA Max	Lim. AIA Min	Lim. AIA Median
500 mg/Nm^3	500 mg/Nm^3	200 mg/Nm^3	500 mg/Nm^3

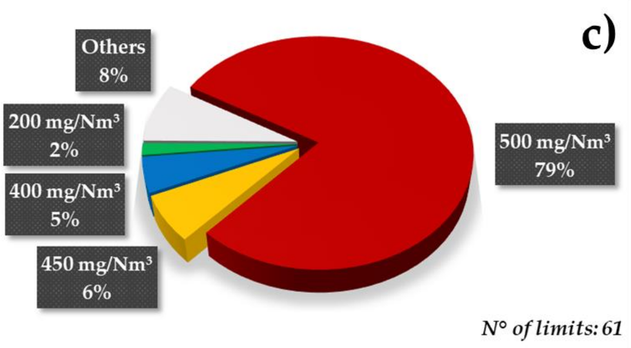


Figure 3-24. **a)** Measured concentrations values of sulfur oxides (SO_x), compared to the maximum and minimum permitted limit as stated in the AIA documents, and expressed as mean values; **b)** number of measures collected, maximum, minimum and median values of all measures and permitted limits; **c)** categories of permitted limits reported in most occurring ranges.

In this case, it is easily noticed the scarcity of data, limited to only 62 values. This fact is related to particular concessions among environmental authorizations which do not require the quantification of SO_x when natural gas is employed as fuel for the spray-drying and firing processes. However, a legal limit is usually in force, in 79% of cases equal to 500 mg/Nm^3, as maximum value. Thus, the measures of the sample will certainly come from those ceramic tile factory which have judge necessary the assessment of sulfur species due to problems related to odor or to the presence of high sulfur impurities in raw materials. In fact, even if the entirety of industrial installations adopts natural gas to feed ceramic kilns, concentration data for sulfur oxides are quite high, with a 60% of values above the most rigid limit and 49% above the mean. In addition, the strong closeness of the mean and median values expresses an almost perfect symmetry in the distribution of data.

All these observations suggest that the presence of sulfur oxides, represented mainly by sulfur dioxide (SO_2), is an undeniable reality and actions shall be undertaken trying to restrain and reduce the amount of this pollutant at the atmospheric emissions from ceramic tile factories.

3.3.5. *Conclusions*

Data on atmospheric emissions concerning the three most impacting stages of the production process of ceramic tiles have been presented in this section. Concentration values have been compared to legal limits enacting at national level in Italy and a discussion has been conducted on the actual emission performance and standards represented by the best available techniques.

Even if supported by an optimal compliance of permitted limits, the most characteristic pollutants of ceramic tile manufacturing, that are particulate matter and fluorine compounds, can represent a serious threat of pollution and easily get out of control if not properly contained. The exponential-alike trend of these pollutants, however, shows also that the good maintenance practice of filtering devices and the proper management of production processes are the key factors in achieving an optimal environmental performance, in line with standards reported inside the ceramic BREF. On the other hand, other pollutants as nitrogen and sulfur oxides and volatile organic compounds, including aldehydes, display more constant distribution of values. This is certainly an indication of the high variability of the sample. Furthermore, this fact suggests that the solutions to implement emissions reduction of such pollutants will be different from the case of particulate matter and fluorine compounds and probably not related to the increased efficiency of abatement techniques. Conversely, the solution is to be found in a more careful selection of raw materials, aimed more at the improvement of the environmental performance, rather than at meeting aesthetic requirements, to which the market often falls victim. After all, this is what has been done in the case of lead. The substitution of this element in ceramic glazes has not led to any particular negative impact on sales while, on the contrary, an effective improvement in environmental performance is almost always appreciated and rewarded by society (Berrone, Fosfuri and Gelabert, 2017). As an example, the adoption of low-sulfur containing clays, the reduction in the use of organic or sulfur-containing additives and inks dispersed in organic media and the selection of pigments containing safer heavy metals are all action that can contribute to improve the sustainability of the manufacturing processes.

It shall be highlighted as the data reported here can be an important instrument for the revision of the ceramic BREF. In fact, the description of the environmental performance of one of the largest ceramic clusters in Europe can be extremely useful in defining the current level of technology in the ceramic industry and new emission standards associated to the best available technique. For example, the future versions of the ceramic BREF shall consider specific emission thresholds for volatile organic compounds and aldehydes and report alternative techniques and materials involved in the decoration process of ceramic products.

Finally, it is important to emphasize that beyond the most modern technologies and the most up-to-date environmental regulations, the good maintenance of manufacturing units and the interest in safeguarding the health of workers and the environment are probably the most important factors in ensuring the sustainability of industrial production.

3.4. Assessment of the recycling practice from the Italian ceramic tile sector

Along with the evaluation of the atmospheric emissions, during the present PhD project, the recycling practice from the Italian ceramic tile sector has also been investigate over time.

Ceramic has always had a remarkable role in the history of the Italian peninsula and across centuries of outstanding artistic production, craftmanship has nowadays evolved into an important industrial sector. Even if entailing vast use of mechanic operations and digital controls, the production process of ceramic commodities is still founding on the same principles, that are the combination of clays and other minerals to afford through shaping crude and fragile semi-finished products which are consequently consolidated by firing at high temperatures. Thus, ceramic experts were able to reach through time high level of efficiency in the exploitation of natural resources and in the yield of industrial production processes. For this reason, the recycling of materials in ceramic tile production is not a recent issue and the level of performance achieved among factories is already significant, as testified by the rich literature related to this sector (Busani, Palmonari and Timellini, 1995; Bonvicini, Fregni and Palmonari, 2006; Timellini, Resca and Bignozzi, 2016; E. Rambaldi *et al.*, 2018; Boschi *et al.*, 2020; Resca *et al.*, 2021).

On the other hand, however, the continuous innovation in the aesthetic and technological aspects of the products demanded by the market, have over the years led to the adoption of natural raw materials characterized by an increasingly rigorous mineralogical composition. As a result, locally available raw materials were abandoned in favor of more expensive, purer or higher-performance resources, leading to an increased use of transport means (Dondi *et al.*, 2021). A consequence is the overexploitation of albitite mines in Turkey, a feldspar used as a high-value flux for porcelain stoneware due to its large amount of low-melting sodium oxide (Na_2O) (Dondi, 2018). Contrarily, the presence of iron impurities (Fe_2O_3), affecting desirable light tones of ceramic bodies with darker hues, has led in the past to the abandonment of clays quarries in Italy, with the collateral adoption of clays coming from Eastern-Europe (Ferrari and Gualtieri, 2006; Andji *et al.*, 2009; Dondi, Raimondo and Zanelli, 2014).

Such a strong dependence on imported raw materials implies a large use of truck and ship transport, aggravated also by the lack of efficient logistic corridors by rails to nearby countries. As a final result, this contributes to increase materials supply costs and carbon dioxide emissions. Besides, it must be pointed out as the dependence for materials supply to singular countries should never be conceded, which implies an economic dependence being excessively exposed to social and political events.

In this work, a vast quantity of data was collected among Italian ceramic tile producers with the aim of illustrating the evolution of various environmental performance indicators during the last decade. In particular, the indicators discussed in the following sections are related to water consumption, waste production, recycling factors of waste and the different recycling layouts, differentiating between the open and closed loop recycling perspectives.

However, the overused distinction between the just mentioned recycling layout is not always effective. In fact, it is not possible to effectively forecast the negative or positive effect of the external or internal recycling path for any industrial case, as it will be demonstrated in the present work. Nonetheless, it was decided to offer here a proper description of recycling paths for ceramic tile factories in order to derive a sort of basic scenario for recycling strategies in this industrial sector.

3.4.1. *Methodology of data collection and analysis*

The calculation procedure of the performance indicators presented in this section was based on the same sample of data addressed in **section 3.2.1**, where the evolution of the atmospheric emissions from ceramic tile factories has been treated. The data collection, the number of factories of the sample and the subdivisions of the different production layouts was the same as in the mentioned case and, thus, for a more detailed discussion of these details, please refer to the cited section.

However, in the present case, the years under assessment covered a shorter time period, from 2013 to 2020, as a consequence of the absence of certain information related to previous years that prevented the calculation of the performance indicators. The wastes considered are those coming from inner production lines of ceramic tile factory, related with raw material exploitation. Water has been treated separately, in a proper section, while solid waste include unfired (S_{uf}) and fired (S_f) scrap, exhausted lime (EL) and ceramic sludges (CS) coming from water depuration and mechanical surface treatment operations.

In order to carry out a faithful description of the recycling practice inside ceramic tile factories, the following recycling indicators have been designed:

- C_w: annual water consumption [1000 m^3/year], obtained as arithmetic mean of values communicated by factories.
$$C_w = \frac{\sum_{i=1}^{i=n} C_{w,i}}{n}$$
- D_w: annual water demand [1000 m^3/year], obtained as arithmetic mean of values communicated by factories.
$$D_w = \frac{\sum_{i=1}^{i=n} D_{w,i}}{n}$$
- R_{sw}: recycling factor for solid waste [%], obtained as weighed mean of values communicated by factories, according to total amount of waste produced by each factory ($W_{out,i}$).
$$R_{sw} = \frac{\sum_{i=1}^{i=n} R_{sw,i} \, W_{out,i}}{\sum_{i=1}^{i=n} W_{out,i}}$$
- R_w: recycling factor for water [%], obtained as weighed mean of values communicated by factories, according to annual water consumption of each factory ($C_{w,i}$).
$$R_w = \frac{\sum_{i=1}^{i=n} R_{w,i} \, C_{w,i}}{\sum_{i=1}^{i=n} C_{w,i}}$$
- BP_{sw}: percentage of recycled solid waste [%] inside the formulation for the ceramic body suspension, obtained as weighed mean of values communicated by factories, according to total amount of spray-dried powder produced by each factory.
$$BP_{sw} = \frac{\sum_{i=1}^{i=n} BP_{sw,i} \, SP_i}{\sum_{i=1}^{i=n} SP_i}$$
- BP_w: percentage of recycled water [%] inside the formulation for the ceramic body suspension, obtained as weighed mean of values communicated by factories, according to total amount of spray-dried powder produced by each factory.

$$BP_w = \frac{\sum_{i=1}^{i=n} BP_{w,i}\, SP_i}{\sum_{i=1}^{i=n} SP_i}$$

where $C_{w,i}$: annual water consumption of the *i*-factory; $D_{w,i}$: annual water demand of the *i*-factory; $R_{sw,i}$: amount of solid waste recycled by the *i*-factory; $R_{w,i}$: amount of recycled water recycled by the *i*-factory; $W_{out,i}$: quantity [ton] of waste produced by the *i*-factory; BP*w,i*: percentage of water recycled inside the ceramic body formulation for the *i*-factory; BP*sw,i*: percentage of solid waste recycled inside the ceramic body formulation for the *i*-factory; SP_i: amount of spray-dried powder produced by the i-factory; n: total number of ceramic tile factories for each year.

Other data regarding the production of waste which have been used to represent the percentage of material landfilled or recycled outside/inside factories, were directly expressed as a percentage calculated from total tons output for each waste considered.

The subdivision in production layouts was maintained in order to minimize the dependence related to dimension, level of technology and peculiar waste output from each plant.

Furthermore, it shall be noted also in this case that in the year 2020 the industrial production has been strongly impacted by the COVID-19 pandemic and the effects on such event on the performance indicator related to that year could be difficult to appraise. In particular, the different lockdown events among municipalities could have had a negative impact on the transport and exchange of resources and waste, thus preventing more effective recycling opportunities.

3.4.2. Management of water

Water is extensively used in the production of ceramic tiles, both as a raw material in the preparation of the ceramic slurry or glaze suspensions, or as a cleaning supply to wash out ceramic powder from the dustiest working environments as, for example, spray-drier locations. Further, water is also adopted as working fluid in squaring and smoothing machineries to contain dust emission and to dissipate generated heat. In **Figure 3-25**, the average annual water demand (D_w) and consume (C_w) and the average amount of recycled water displayed by the three production layouts is reported over a time span of eight years.

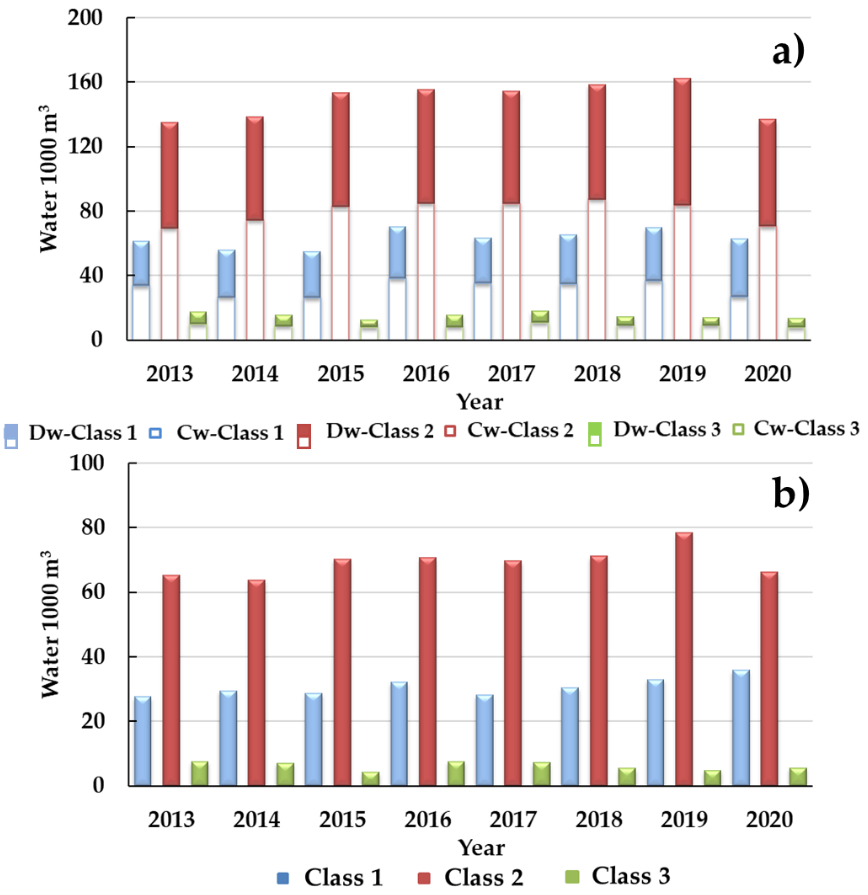


Figure 3-25. a) Annual demand (D_w) and consume (C_w) of water and **b)** amount of water recycled by the three production layouts from year 2013 to 2020.

Water consumption (C_w) indicates the amount of water required to restore the part lost during evaporation events in the spraying and drying phases and during tile decoration. Water demand (D_w), conversely, simply represents the quantity involved in the production process, while the difference between water demand and consume values (**Figure 3-25 b**) represents the quantity of water internally recycled.

It can be seen that the three different classes, depending on the different production layouts, require particularly different amounts of water. In general, factories involved in the production of spray-dried powder for third parties (class 2) have the highest water demand, the highest consumption and the highest recycling. On the other hand, plants with a production cycle without raw material preparation and spray drying procedure (class 3) are characterized by the lowest values. It should be noted that the water demand data do not seem to be consistent with the production data in **figure Figure 1-2**, which show a significant decrease after 2017. Indeed, during 2018 and 2019, both water demand and water consumption increased despite the decrease in tile production. This evidence is probably related to the increased number of finishing operations carried out after firing, which in turn is closely linked to market trends.

Thus, even with a decrease in production, the increased market demand for rectified tiles and smooth ceramic surfaces resulted in an increased demand of water. Fortunately, this increment is also followed by a corresponding increase in the recycling of water, thus highlighting that water recycling during ceramic tile production is a well-established practice.

3.4.3. Production of solid waste

The assessment on solid waste has been focused on those mainly produced in tiles production plants. The four wastes analyzed are unfired (S_{uf}) and fired (S_f) scrap, exhausted lime (EL) and ceramic sludges (CS).

While unfired scraps are fully recycled in ceramic body preparation stage, fired ones can be recycled in limited amounts. In fact, the sintering of ceramic material during firing leads to alteration of mineral phases of raw materials, bringing to breakdown of the aluminum silicate reticule of clays and creating new phases as, for example, mullite, characterized by high hardness and refractory behavior. This latter consideration applies also for ceramic powder contained in ceramic sludges coming from surface treatments operations, as squaring and polishing of fired pieces. On the other hand, this is not the case for other sludges mainly composed by unfired ceramic powder. However, in the present assessment these latter two kinds of waste have been considered together as ceramic sludges (CS). Differently from the three just mentioned cases, the generation of exhausted lime is by far less abundant, differing by two orders of magnitude. In fact, lime is not a raw material intended for tiles production, but it is still an important component involved in the purification of exhausted fumes from kilns, as described in detail in **section 1.4**. Exhausted lime is at today hardly recycled and it is, among those presented, the singular refuse entirely destined to landfilling, so often with high costs connected, due to its labeling as hazardous waste by the current legislation (Council Directive 91/689/EEC, 1991).

Figure 3-26 illustrates the annual average solid waste production for the three different production classes, expressed as kg on ton of tiles produced (kg/ton), and reported over a time span of eight years.

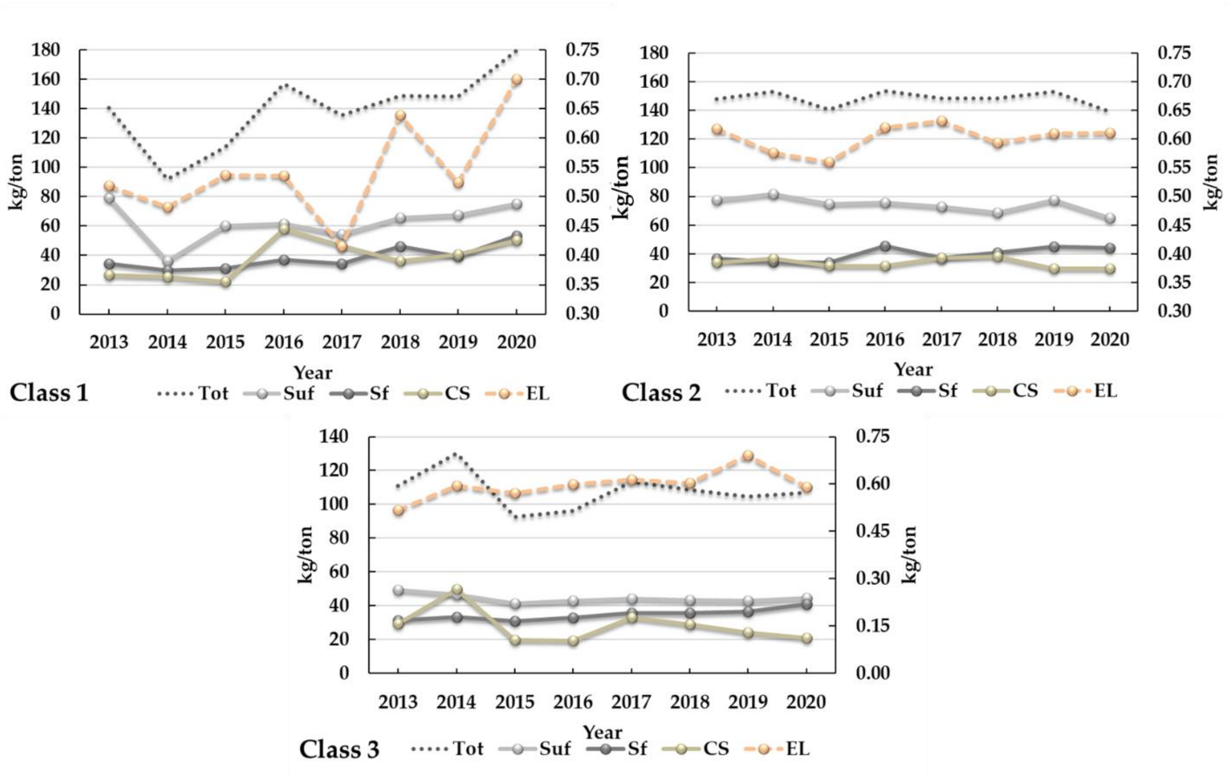


Figure 3-26. Production of solid waste for the three production classes from year 2013 to 2020. S_{uf}: unfired scrap, S_f: fired scrap; CS: ceramic sludge; EL: exhausted lime (right *y*-axis); Tot: total sum of waste (S_{uf} + S_f + CS + EL).

The lowest production of unfired scrap (S_{uf}) is exhibited by class 3 with a mean value of 44.4 kg/ton over the whole period, followed by class 1 with 62.4 kg/ton and, finally, by class 2 with 74.1 kg/ton. Such tendency is utterly consistent with the differences in production processes of the three classes. In fact, factories producing an additional amount of spray-dried powder for the market handle higher loads of raw materials compared to factories belonging to class 1, consequently generating a higher amount of unfired waste. Obviously, factories belonging to class 3, which do not exhibit the raw materials preparation stage, are characterized by the lowest generation of this waste.

Concerning fired scrap (S_f), classes 1, 2 and 3 all display similar mean values of 38.2, 39.8, 34.8 kg/ton respectively, because both the firing process and final operations are essentially performed with no major differences by all the three production layouts. Same behavior occurs for exhausted lime production (EL), where an average value ranging between 0.54 – 0.60 kg/ton has been determined. Same observations apply to the production of exhausted lime (EL), where mean values for the three cases fell in the range between 0.54 and 0.60 kg/ton.

Ceramic sludge (CS) shows a trend which is strongly related to the production layout, as in the case of unfired scrap (S_{uf}). The highest value is generated by factories belonging to class 1, with a mean of 38.2 kg/ton, followed by class 2 and 3, with 33.5 and 28.1 kg/ton as mean values, accordingly. In the latter case, the lower production of ceramic sludge is due to the absence of the grinding and spray-drying stages, which make an important contribution in the generation of this type of waste.

Finally, it is pointed out that, although with important fluctuations, class 1 seems to represent an increasing waste production over time, while trends for the other two classes seem to remain constant. It is difficult to understand what this difference is related to, whether more to the reduced sample of companies for this production class, or to other particular factors. What is certain, however, is that the most important contribution to the total amount of waste produced is, in all cases, the unfired scrap, followed by fired scrap and then, ceramic sludges. It appears, therefore, that actions aimed at increasing the strength of crude tiles or decreasing the mechanical stresses to which these are subjected, can make an important contribution to the total reduction of waste production during the entire manufacturing process.

3.4.4. Recycling factor of solid waste and water

Figure 3-27 illustrates the recycling percentages [%] of solid waste (R_{sw}) and water (R_w) for the three production classes, reported over a time span of eight years. In the current assessment, these two indicators represent the amount of water and solid waste recycled both within and outside ceramic tile factories. Thus, they give an indication about recycling capacity of different production layouts. In fact, some industrial realities are unable to recycle much material, choosing landfilling or external recycling solutions on variable extent, while others are able to host inside production processes higher amount of waste than those produced.

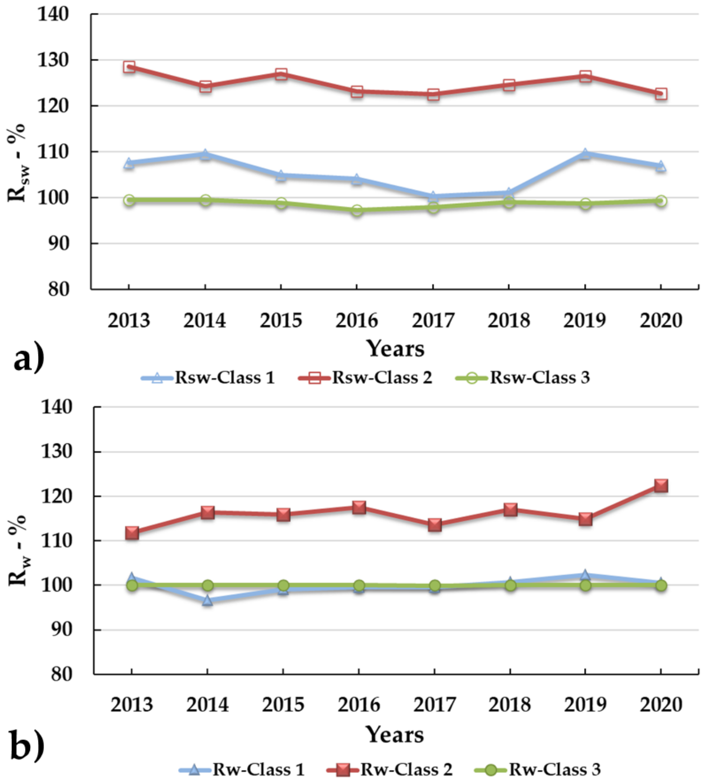


Figure 3-27. Recycling factors of **a)** solid waste and **b)** water for the three production layouts from year 2013 to 2020.

A high tendency toward recycling practices is demonstrated by data in **Figure 3-27**. Almost in all cases, values reach the maximum of 100 %, meaning that, as a rule, a nearly absolute recycling of resources is accomplished. Values beyond maximum are reasonable if also considering the recycling of materials coming from outside ceramic factories.

As expected, class 2 displays the highest score for the two indicators, with a maximum of 122.5% (2020) and of 128.7% (2013) for the recycling of water and of solid waste, respectively. The excess production of spray-dried powder gives opportunity to welcome great quantity of secondary resources in the ceramic body formulation stage. Class 3, otherwise, cannot attain such efficiency because the chance to recycle materials up to such percentages is prevented for this production layout. Accordingly, most of their wastes is recycled outside factories, by those belonging to class 1 and 2. However, class 3 still manages to master the complete recycle of water, showing values equal to 100% on the whole time-period, while for solid waste the maximum obtained value has been found in 2013, with 99.6%.

Values of recycling of solid waste for class 2 maintain pretty much constant during the years, while it seems that water reutilization practices have been increasing over time. For class 1 trends are opposite. Water recycling always maintains around 100%

whereas that of solid waste manifested a continuous decrease until 2018, when trend reversed, touching with 109.8% in 2019 the highest value of the whole time-period. However, as it will be shown in the following section, the amount of waste recycled by these factories seems to be currently increasing.

3.4.5. Recycling factor of solid waste and water in the ceramic body preparation

In order to realize how waste and water are recycled inside ceramic tile factories, it is certainly interesting to express the percentage of recycled solid waste inside the formulation for the ceramic body suspension. This preparation stage, in fact, is the unit of whole production process which is able to host waste materials at highest amounts. Unfired broken tiles and powder from filtering processes ahead the firing stage, can theoretically be reintroduced in ceramic mills with water to almost any extent because of the unaltered mineralogical structure. Exceptions are possible with unfired tiles which have been subjected to surface decoration treatments by applying frits and pigments and with fired ceramic material. Recycled water can as well be introduced in ceramic slurry preparation in high quantities. In fact, this process is not particularly sensitive to the presence of little impurities and no extreme purity is demanded as, for example, it happens for the preparation of glazes slurries. In this last case, impurities can lead to minor but critical defects on the surface of tiles. On the contrary, for ceramic body of utmost importance are the rheology properties of the slurry, which can be finely tuned with little amounts of additives.

Figure 3-28 illustrates percentages by weight for solid waste (BP_{sw}) and water (BP_{w}) recycled inside the formulation for the ceramic body suspension, reported as weighted value for class 1 and 2 over a time period of seven years. Because of the absence of data for 2013, it was not possible in this case to provide indicators for this year. Further, class 3 is not represented because factories belonging to this class do not include milling and spray-drying steps in their production process.

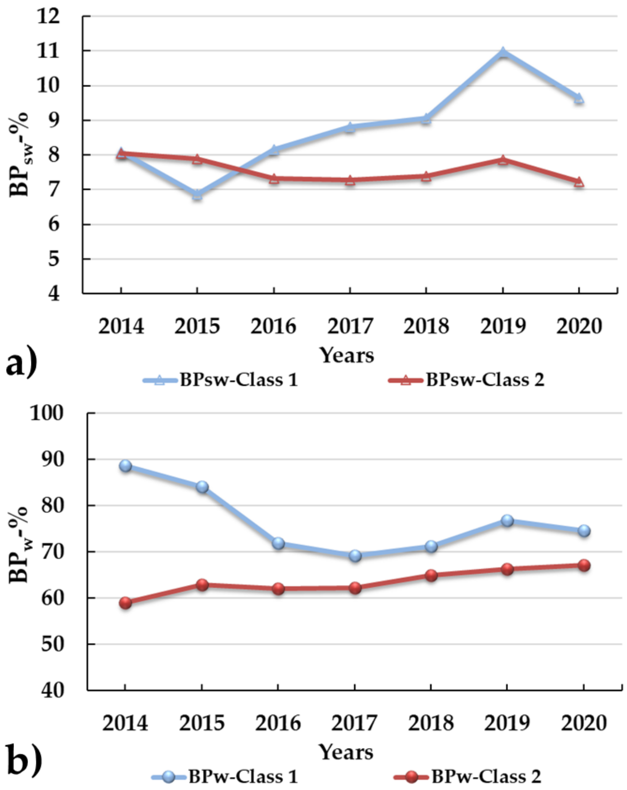


Figure 3-28. Recycling factors of **a)** solid waste and **b)** water in the formulation of the ceramic body liquid suspension, for classes 1 and 2 from year 2014 to 2020.

It is easy to see how factories belonging to class 1, almost in any case, exhibit higher values compared to those of class 2, for both recycling indicators. This fact does not mean that first ones are able to recycle more material than latter ones. Simply, because of the far higher amount of spray-dried powder produced by factories of class 2 for the same waste production, if tiles production is assumed equivalent, these are normally limited to lower percentages of recycled material inside the ceramic suspension, if compared to those belonging to class 1.

The trend for the recycling of solid waste for class 1, with the exception for the year 2015 (6.9%), displayed a promising progression, starting with an 8.1% of waste recycled in 2014 to a 11.0% in 2019, followed then by a drop in 2020. Class 2, on the other hand, performed a recycling percentage for solid waste of 8.0% for 2014, followed by a progressive decreasing until 2017 (7.3%) and then, by a return to original values, with 7.9% for year 2019. It is hard to explain such contrasting values exhibited by class 1 factories. However, as seen in other sections of the present work, such trends could be to certain extent justified by the minor availability of data representing class 1, together with high fluctuation in values presented by single factories.

As regards recycling of water, trends are almost opposite. For class 1, values has decreased through years, reaching a minimum of 69.2% in 2017. However, trend is increasing in the last period, with a 77.2% of water recycled for year 2019, if exception is made for year 2020, when the outburst of COVID-19 pandemic altered the production. For class 2, otherwise, values are more constant and slowly but constantly increasing with a 59% and a 67.1% of water recycled for years 2014 and 2020, respectively.

3.4.6. Internal and external recycling paths

The recycling of water and solid waste has been presented in the previous **section 3.4.4**, considering however the recycling percentages as arising indistinctly from internal and external reutilization of resources. Thus, it was not possible to appreciate differences in these two recycling paths. Actually, such distinction is quite essential.

In fact, even if a second life chance for materials is still awarded and even if external reutilization can empower important savings for raw materials in other sectors, in certain cases such procedure could negatively affect the environmental and economic sustainability of ceramic tile factories. Internal reutilization of resources can provide some important advantages. In fact, water and solid waste can easily be reinserted inside production processes with minimum loss of material, lower bureaucratic constraints and zero economic losses. On the other hand, relying on external entities for resources valorization could imply a series of drawbacks. To be reinserted in other industrial production cycles, water and solid waste can sometimes be subjected to chemical or mechanical treatments with loss of material and with related economic costs. Other costs and bureaucratic burdens, as well as negative effects on the environment, are linked with transport pathways, usually by lorries and/or trains, on which external recycling must rely.

However, it is not possible to forecast the negative or positive effect of external or internal recycling path for any industrial case and the overused distinction between open-loop and closed-loop recycling should be avoided. In fact, as for example regarding the loss of material, addressed for open loop recycling strategies, it can actually happen also for internal reutilization, as it has been shown with the recycling of fired tiles in ceramic body preparation, because of the need of a high fine grinding pretreatment. Again, open-loop recycling could sometimes offer recycling paths where wastes are awarded with added value, causing the internal reutilization of materials to be not so profitable. Nonetheless, it was decided to offer here a proper description of recycling paths for ceramic tile factories in order to derive a sort of basic scenario for recycling strategies in this industrial sector.

In **Table 3-1** the total amount of unfired and fired scrap, exhausted lime and ceramic sludges produced by ceramic tile factories, expressed as average percentages by weight of each waste in the period 2013-2020 is reported as function of the different recycling pathways, identified as internal and external reutilization or as landfilling.

Table 3-1. Final destination for the annual total amount of waste [%] produced by ceramic tile factories (S_{uf}: unfired scrap; S_f: fired scrap; CS: ceramic sludges; EL: exhausted lime). Averages were calculated considering the annual values from year 2013 to 2020.

	Internal Origin - Internal Use [% wt.]				**Internal Origin - External Use [% wt.]**				**Landfill [% wt.]**			
	S_{uf}	**S_f**	**EL**	**CS**	**S_{uf}**	**S_f**	**EL**	**CS**	**S_{uf}**	**S_f**	**EL**	**CS**
Class 1	68.5	20.8	8.8	59.9	31.5	77.8	2.7	39	0	1.4	88.6	1.1
Class 2	89.2	16.9	2.6	54.3	10.8	82.5	1.8	44	0	0.6	95.6	1.7
Class 3	2.9	0.1	0	1.2	97.1	98.4	17.2	97	0	1.5	82.8	1.8

How it is easier for factories to recycle unfired scrap (S_{uf}) is efficiently proven in the table. Factories of class 1 recycle internally almost the 70% of wastes while those of class 2 almost the 90%. For class 3, because of the absence of the ceramic body preparation step, almost the entirety of wastes has to be recycled externally. However, some portions of scrap are still managed, probably those linked to glazes and frits.

Fired scrap (S_f), on the other hand, is especially recycled externally to factories because of the aforementioned difficulties in reutilizing high quantities of such waste at one time inside the ceramic body preparation step, as a consequence of its hardness and its consolidated nature.

As suggested above, exhausted lime (EL) is almost totally landfilled, because of the bureaucratic hindrances in its recycling linked to its labeling as hazardous waste. The few tons registered for recycling are probably intended as reutilization in hot fumes depuration. However, several works have already demonstrated the possibility of reusing this type of waste, even if only at an experimental level (Bernardo, 2008; Ponsot, Falcone and Bernardo, 2013).

Finally, the recycling percentages for ceramic sludges (CS) lies somewhere in between the cases of unfired and fired scrap. In fact, because of the consolidated crystalline structure of solid waste coming from surface treatments, only a minor amount of it can contribute to internal use while the waste coming from the treatment of different water sludges can be easily and efficiently recycled internally.

An alternative representation of data is reported in **Figure 3-29**, where the total amount of solid waste produced within ceramic tile factories has been divided according to the percentages of the internal and external recycling or landfilling solution, calculated on yearly basis for a time period of eight years.

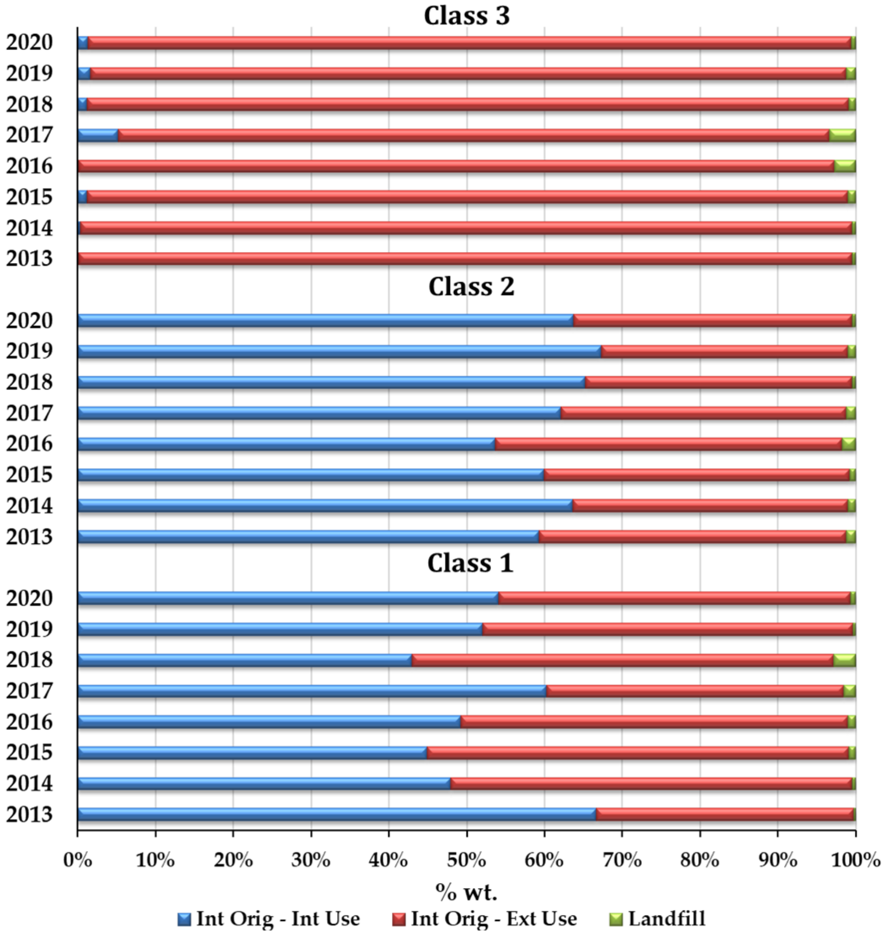


Figure 3-29. Percentages by weight of the solid waste produced by the three production layouts as function of final destination (internal and external recycling and landfilling), from years 2013 to 2020 (Int. Orig. – Int Use: internal origin – internal use; Int. Orig. – Ext Use: internal origin – external use).

The first thing to note is how it is actually decisive the ceramic body preparation step for internal recycling of resources. Indeed, class 3 factories rely almost exclusively on external recycling routes, transferring waste to other ceramic factories or even different industrial sectors for recycling purposes. However, even with no such production stage, class 3 shows minimal percentages of landfilling. Regarding classes 1 and 2, the percentages are actually quite similar, even if class 2 demonstrated a slightly higher tendency to internal recycling during the overall time period, with the only exception of year 2013.

Another evidence to highlight here is the difference in the corresponding trends. Class 2 factories seem to rely less and less on external recycling of materials over time, as the percentage of internal reuse of materials has been increasing since 2016. Conversely, for class 1, no precise trend can be noticed, although there was a substantial increase in internal recycling over the last three years.

Finally, it should be emphasized as also for class 1 and class 2 recycling is a prominent tendency in materials disposal, being the quantity of material destinated to landfilling quite low over the whole period under assessment. In this manner, ceramic factories are able to prove the hard work done during the years in order to maintain the sustainability of value chain of raw materials and resources.

3.4.7. Conclusions

The large amount of data collected for the present work made it possible to develop several performance indicators and to outline some important trends in waste generation and management of resources. The rationale beyond that was to provide a portrait of the waste management practice at industrial level, in this case the one acting in the Italian ceramic tile district. The description of a sort of basic scenario will enable the ceramic sector to direct future actions toward an improved competitiveness by avoiding futile economic losses linked to lack of information and recycling inefficiency and to the pursuit of blind environmental policies. In fact, it is very important to find out how the generation of waste can be tackled, both in term of environmental and economic sustainability, and to find solutions to a problem which is often generated by shortage of communication and trading channels among industries rather than by an inadequate level of technological maturity.

This research work highlighted the following aspects of the resource management implemented in the Italian ceramic tile sector:

- Class 2 is the production layout involving both the highest consume of water and waste production. That is mainly related to spray-dried powder production, the most impacting step of the whole manufacturing cycle in term of resource consumption. However, this same working step is also responsible of the greatest percentages of water and solid waste recycling. As a consequence, in order to improve the sustainability of the whole process, factories should invest to improve efficiency of such plants, aiming at reducing water and energy consumes and increasing percentages of second-hand raw materials involved in the production of the ceramic body.

- Class 3 is the production layout characterized by the lowest level of self-sufficiency. Although the impact on resource utilization is low for factories belonging to this class, they are not able to rely on the internal utilization of waste, preventing a reduction in resource migration. In order to reduce their environmental impact, such factories must be located near class 2 factories, which can both furnish and accept material from them. Otherwise, excessive reliance on road transport can be detrimental for the economic and environmental sustainability of this industrial reality.

- Exhausted lime is almost totally landfilled and almost no recycling options can free ceramic factories from the economic and bureaucratic burdens linked to the production of such refuse. For this reason, scientific research shall proceed with the aim of making such inertization and recycling opportunities feasible and efficient. It is pointed out here that, because of the poor quantities of lime landfilled, even very scarce percentages of adoption as a raw material could prevent additional generation of this waste.

- Based on the illustrated trends, the improvement of internal recycling has been demonstrated as fairly achievable at the current level of technology. In fact, especially through the ceramic body preparation step, it is possible to welcome great quantities of solid waste and water inside ceramic suspensions. However, it can be seen how improving the outcome of the firing process can make a major contribution to the reduction of that kind of waste, the fired scrap (S_f), which is more difficult to recycle due to the milling process required and the maximum limit at which it can be incorporated into the ceramic body.

It is important to highlight here, as the constant revision of these data and indicators will be of great importance in describing the efficacy and true impact of circular economy policies adopted along the years in industry at national and European level. For the future, the common ambition of all different industrial sectors shall be an interconnecting web of manufacturing entities governed by a free exchange of materials and information to achieve a complete exploitation of resources together with theoretically null yield of wastes. In a globalized world where goods production and services providing are easily expanding worldwide, industrial manufacturing sectors cannot be bound to old market practices and mute communication behavior. In other words, to a free market of goods a free market of waste and information shall follow, to grant industries to easily sustain themselves with an increased economic competitiveness and improved environmental sustainability.

3.5. Development of new ceramic engobes with glass residues

Another important activity carried out during this thesis work was the development of new ceramic engobes by using waste glass as a more sustainable alternative to a white zircon frit used as fluxing agent inside commercial engobes. Glass, in fact, shares some characteristics with ceramic frits and could potentially be employed in the formulation of ceramic engobes and glazes, contributing to save important amounts of material from landfills and, at the same time, to reduce the energy expenditure and the raw material consumption for the synthesis of ceramic frits.

Globally, glass waste represents about 5 wt.%, while in higher income regions of the globe, such as Europe, glass waste accounts for 8 wt.% of total waste production. Among glass waste sources, bottles and containers are responsible of almost 80 wt.% of discarded glass material, while only 20 wt.% comes from durable goods (Advancing Sustainable Materials Management, 2020). These latter are described as products that last at least three years. An example of glass waste belonging to such category, which is causing increasing concern lately, is glass from the dismantling of solar panels. In both cases, the glass is the soda-lime-silica type, differing only in the presence of minor constituents affecting collateral properties, such as, colour and light reflection (Vogel, 1994). However, while the recovery of glass containers is a long-known and widely adopted practice, the recycling of solar glass panels is still a minor reality, principally due to the still scarce collection of end-of-life solar panels for which an average lifetime of 25 years has been estimated (Chowdhury *et al.*, 2020). In fact, only in the late 1990s the technology started to obtain certain relevance. Recently, the European Union has included solar panel waste in the new Waste of Electrical and Electronic Equipment (WEEE) directive in order to tackle the continuous growth of this waste and its improper dumping, by charging European producers with the responsibility to collect and dispose of the expired modules (Directive 2012/19/EU of the European Parliament and of the Council). Therefore, appropriate management of such waste is becoming increasingly urgent and the scientific community is mainly focusing on the development of competitive and sustainable recycling paths (Cucchiella, D'Adamo and Rosa, 2015). Most solar panels are produced from crystalline silicon while a minor share of the market includes thin-film technologies involving cadmium telluride (CdTe), amorphous silicon and CIGS cells (Sander, 2007). However, despite the variety, recycling strategies are analogous. Dismissed solar modules can be chemically, mechanically or thermally treated in order to separate the precious conductive components and the glass fraction, which commonly accounts up to 65-75 % of the modules' weight (Sander, 2007; *Snapshot of Global PV Markets 2022*).

As detailed reported in **section 2.2.3**, there are many examples of the utilization of glass scraps in the field of traditional ceramics. Despite the abundance of scientific production in these fields, examples of recycling in ceramic engobes are rarely found in the literature (Lazaro *et al.*, 2012; Dal Bó, Bernardin and Hotza, 2014; Nandi *et al.*, 2015). An engobe is a layer that is applied between the ceramic substrate and the upper glaze layer of tiles in order to attenuate differences in the physical and chemical properties of the two components, in particular, in their thermal expansion, fusibility and colour. For such reasons, the main features characterizing engobes are the coefficient of thermal expansion (CTE) and the whiteness (expressed as L*, according to CIELAB colour space). Specifically, differences between the CTE value of the ceramic substrate and the upper glaze layer can result in improper coupling with a series of undesired drawbacks. When the CTE of the glaze is lower than that of the body, the glazed surface is under compression, with the risk of peeling effects or turning the surface of the tile convex. On the contrary, when the CTE of the glaze is too much higher compared to that of ceramic substrate, the glaze is under tension, resulting in concave tile's surface or in crazing effects (Peterson *et al.*, 2007). Whiteness of engobe, otherwise, is fundamental to conceal the usually darker tones of ceramic substrates through transparent glazes in order to provide a white ground for all series of digital decorations.

It was found in scientific literature a promising example of a total replacement of the frit (20 wt.%) inside a ceramic engobe formulation using a mixture of soda-lime-silica glass (Dal Bó, Bernardin and Hotza, 2014). Thus, the aim of the present research work was to substitute the opaque white frit in a commercial engobe used for porcelain stoneware tiles. The percentage of frit in the engobe formulation was 20 wt.% and was evaluated its substitution by two different waste glasses, one from a solar panel and the other from a bottles manufacturer. However, differently from the approach of Dal Bó *et al.*, 2014 and Nandi *et al.*, 2015, who formulated engobes starting from natural or synthetic raw materials and adding recycled glass and ceramic sludge, in this work the engobe composition was kept constant and only the frit was, partially or totally, substituted. Waste glasses were used as more sustainable alternative of the fluxing agent while kaolin was adopted to reduce the impact on colour and coefficient of thermal expansion of new engobe formulation, without excessively impacting on the rheology of engobe suspensions (Lagaly, 1989). New engobe formulations were obtained in two different forms, as tablets and thick layers applied on porcelain stoneware tiles, in order to evaluate the impact of added materials on the colorimetric coordinates (CIEL*a*b*), the coefficient of thermal expansion (CTE), water absorption and shrinkage of samples. In addition, in the samples in which the frit was totally substituted with glass, the influence of temperature on the firing behaviour of engobes was studied.

Starting from the composition of a commercial engobe, two waste-based engobes, in which the frit portion has been substituted by waste glasses, were developed. The one with GM glass and kaolin (10GM10K), is proposed as a more sustainable alternative for the commercial engobe, while the other, only with SP glass (20SP), has a lower firing temperature and is suitable to be used in ceramic bodies and glazes with higher CTE values.

3.5.1. *Materials and methods*

Transparent glaze (TG) and engobe for porcelain stoneware tiles (Std Engobe), kaolin, opaque white frit (Frit) and the engobe without the frit fraction (Engobe w/Frit) were provided by Esmalglass Portugal S.A. Two glass wastes were used, one resulting from the dismantling of solar panels (SP), provided by Sogliano Ambiente (Italy), and the other resulting from the glass bottles manufacturing process (GM), supplied by BA Glass (Portugal). Unfired porcelain stoneware tiles (65x32.5 cm and 9.2 mm height), were provided by Aleluia Cerâmicas (Portugal).

3.5.1.1. Characterization of glass residues

The chemical composition of the two glass residues (SP and GM) was determined through X-ray fluorescence technology in a Philips X'Pert PRO MPD spectrometer. Values of loss on ignition (LOI) were also determined at 1000 °C. The granulometric distribution of milled glass was controlled by laser diffraction in a Coulter LS analyzer (LS 230, Fraunhofer optical model). Scanning Electron Microscopy and Energy Dispersion Spectroscopy (SEM/EDS) images were obtained on carbon-coated milled glasses in a SEM Hitachi SU-70, 25kV acceleration voltage instrument. Characteristic thermal parameters of glass residues and frit were determined by hot stage microscope through a Misura® HSM 3.32 Expert System Solutions instrument.

3.5.1.2. Preparation of the suspensions

Commercial engobe (Std Engobe) has in its composition 20 wt.% of frit which has been, totally or partially (10 wt.%), replaced by waste glasses (SP and GM). The influence of kaolin addition (5 and 10 wt.%) was also evaluated in the samples in which the frit was partially replaced by waste. The prepared formulations are presented in **Table 3-2**.

To prepare the suspensions with glass residues and frit, these materials were ball-milled in a Ceramic Instruments S2-1000-M mill with water and alumina balls (waste glasses/frit:water:balls in 1:1:2 weight ratio) until a particle size distribution similar to that of commercial engobe was achieved. Then, the suspensions were sieved at 125 μm in order to remove extraneous materials, observed in the GM waste.

The Brongniart formula was used to calculate the amount of dry engobe fraction in the suspension:

$$W = D\,\frac{(L - 100)}{(D - 1)}$$

Where W (g) is the weight of dry material in 100 mL of slip, L is the weight (g) of 100 mL of suspension and D represents the relative density of the material inside the suspension, in this case considered 2.6 g/cm^3.

Table 3-2. Prepared glaze slip compositions.

Samples	Std	10SP	10SP10K	15SP5K	20SP	10GM	10GM10K	15GM5K	20GM
					(wt.%)				
Std Engobe	100	-	-	-	-	-	-	-	-
Engobe w/Frit	-	80	80	80	80	80	80	80	80
Frit	-	10	-	-	-	10	-	-	-
Kaolin		-	10	5	-	-	10	5	-
SP	-	10	10	15	20	-	-	-	-
GM	-	-	-	-	-	10	10	15	20

The rheological behaviour of the prepared engobe slips was investigated using a NETZSCH Kinexus lab+ instrument, at constant temperature, 25 °C. In particular, the shear viscosity versus shear rate for each engobe suspension was appraised in order to evaluate changes in viscosity and to investigate shear thinning and/or shear thickening behaviours. Engobe suspensions were subjected to rheological testing with a density of 1.45 g/mL, which is the industrial application density of the commercial engobe.

3.5.1.3. Preparation of the samples

The prepared engobe suspensions were applied on the surface of dry porcelain stoneware ceramic tiles using two techniques: glaze die and jet-spraying, see **Figure 3-30**.

Figure 3-30. Jet-spraying (left) and glaze die (right) apparatus deposition of ceramic engobes and glazes.

In the first case (glaze die deposition), the density of the slips was adjusted to 1.65 g/mL by the addition of water. Then, the prepared mixtures were applied, in thick layers, on dry porcelain stoneware tiles using a glaze die with an opening of 0.6 mm. These samples were used for colorimetric measurements and preliminary assessment. In the case of the jet-spraying deposition, the density of the engobe slips was 1.45 g/mL and it was sprayed over the ceramic tile, depositing approximately 5.6 g of engobe per dm^2 of tile.

To assess possible reactions between the added glass residue and the outer glaze layer, in both cases, a transparent glaze was applied on top of the tiles by jet-spraying. The deposited quantity was, approximately, 3.3 g/dm^2. Furthermore, tablets were also produced. For this purpose, the slips were dried overnight in an oven at 120 °C. After drying, the powders were disaggregated and pressed to obtain tablets with 25 mm of diameter. In this case, a Type C Carver Laboratory Press was used and a uniaxial pressure of 400 kg/cm^2 was applied.

The tablets and thick glaze layers were fired at the University of Aveiro, using a Termolab MLR laboratory muffle with the following cycle: (I) heating rate of 10 °C/min until the maximum temperature; (II) 10 minutes dwell at maximum temperature, and (III) cooling rate of 10 °C/min until room temperature.

In order to assess the influence of the firing temperature on the engobe formulations in which the frit was fully replaced by waste glasses (20SP and 20GM), tablets were fired following the same heating cycle but changing the T_{max}, embracing a range of temperature around 150 °C: 1050, 1078, 1108, 1158, 1195 °C as T_{max}.

On the other hand, jet-spraying tiles specimens were fired at Aleluia ceramic factory adopting a 76 minutes firing cycle with a maximum temperature of 1200 °C. Real maximum firing temperatures were determined using Bullers pyrometric rings from Mantec Technical Ceramics.

3.5.1.4. Characterization of the samples

The aesthetic appearance of fired engobe tablets, thick layers and glazed tiles was appraised by determining values of CIEL*a*b* coordinates with a portable colorimeter Konica Minolta Chroma Meter CR-400 (Y: 94.0, x: 0.3130, y: 0.3191 for standard white). Colour differences were estimated using the value of ΔE:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

where for $0 < \Delta E < 1$ the colour difference cannot be perceived by the standard observer; for $1 < \Delta E < 2$ a difference can be perceived only by an experienced observer; for $2 < \Delta E < 3.5$ a difference can be perceived also by an unexperienced observer; for $\Delta E > 3.5$ anyone can perceive a colour difference. Water absorption tests on engobe tablets were carried out following the European standard EN ISO 10545-3. The shrinkage of tablets was determined by measuring changes in their diameter after firing according to the following equation:

$$Shrinkage\ (\%) = \frac{d_{dry} - d_{fired}}{d_{dry}} * 100$$

where d_{dry} represents the diameter of dry tablets and d_{fired} the value after the firing procedure. Evaluation of the thermal expansion behaviour of modified engobes was carried out by measuring the coefficient of thermal expansion (CTE) of fired engobe samples, using a NETZSCH DIL 402 Expedis Classic dilatometer. Crystalline phases ware investigated on fired tablets through X-ray diffraction (XRD), using a PANanalytical XPert PRO diffractometer (Ni-filtered CuKa radiation, PIXcel 1D detector, exposition of 2 s per step 0.02° 2θ at 25 °C). Finally, Scanning Electron Microscopy (SEM) images were collected from broken pieces of fired tiles after polishing procedure.

3.5.2. Results and discussion

3.5.2.1. Characterization of glass residues

Waste glass residues were delivered in coarse fragments (1-10 mm) without being subjected to any pre-treatment (*e.g.* cleaning operation, milling) (**Figure 3-31 a**). Residue SP derives from a dismantling plant of solar panels in Italy, where metal frames, silicon sheets and polymeric junctions, together with electronic apparatus, are separated from the transparent glass. Residue GM comes from a glass bottles manufacturer, and it is composed of glass of different colours, embodying also a minor fraction of glazed ceramic, glass-ceramic pieces, metal, and paper. SEM micrographs of glass residues after milling are shown in **Figure 3-31 b**.

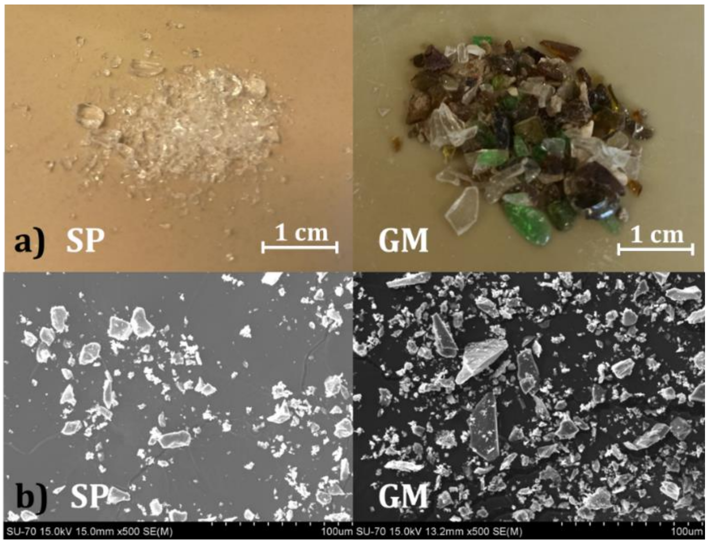


Figure 3-31. a) Glass residues as delivered; **b)** Glass residues after milling (SEM, 15.0 kV, x500). SP: solar panel glass, GM: waste glass mixture.

SEM images show that sample GM, after milling, presents some big glass fragments (around 40-50 μm) with sharp edges dispersed in the mass of fine particles. SP sample reveals glass particles characterized by a more uniform size and shape than GM.

Particle size distributions of milled glass residues are presented in **Figure 3-32** along with the ones of the commercial frit, the engobe without frit (EwF) and kaolin.

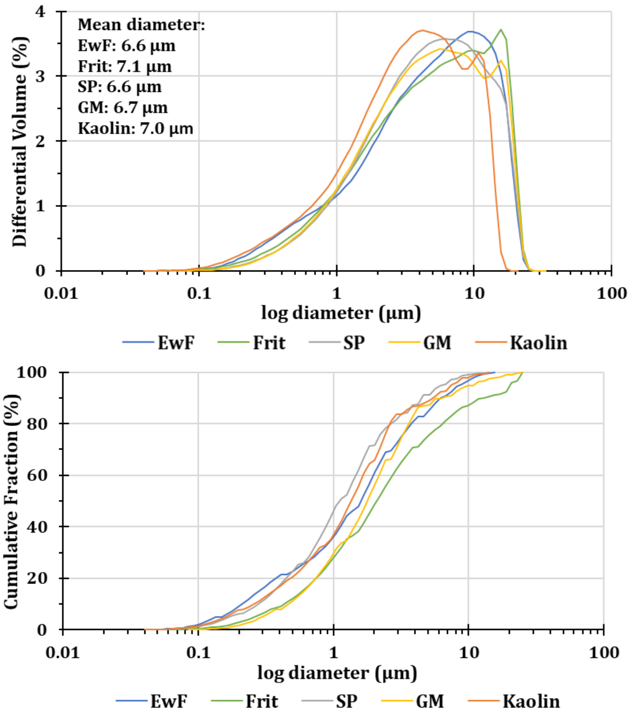


Figure 3-32. Particle size distribution of the glass residues, commercial glazes, frit and kaolin (EwF: engobe without frit).

All the curves are similar in terms of particle size range and medium particle size (6.6-7.1 µm). Kaolin slightly differs from the others, presenting a slightly smaller range of particle size.

Figure 3-33 presents the aspect of pressed raw materials powders (the two glass residues (SP and GM), the white opaque frit (Frit), the commercial engobe (Std) and the commercial transparent glaze (TG)) after being fired, in a laboratory muffle, at 1153 °C on a ceramic support.

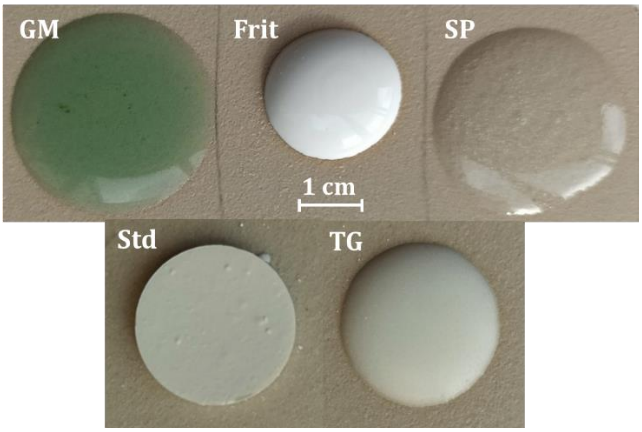


Figure 3-33. Aspect of tablets fired at 1153 °C in a laboratory muffle.

The two glass residues (GM and SP) seem to manifest a similar melting behaviour, being clearly more fusible than the other evaluated materials. However, GM sample, being a mixture of coloured glass, display a strong green hue while SP sample is completely colourless. On the other hand, the three commercial materials (Frit, Std and TG) manifest a quite different behaviour. The standard engobe (Std) is opaque, exhibits a cream colour and a rough surface texture and is the only sample that did not form, at the maximum firing temperature, an amount of liquid phase enough to promote the change of its shape. The commercial transparent glaze (TG) displays an opaque white-cream colour and a slightly rough texture, probably because is not completely transparent and because the thickness of the sample is much greater than the thickness of a glaze layer. The commercial frit exhibits a peculiar melting behaviour, reaching full vitrification and displaying a shiny white colour and a smooth texture but shrinking in diameter while growing in height.

From this preliminary firing test, it was possible to derive some hints on the influence of frit substitution with SP and GM residues. In fact, the transparency of the two glasses, in contrast to the whiteness and higher opacity of the frit, will certainly contribute to lowering the opacity and whiteness exhibited by the modified engobe formulations. Also, due to the proven increased fusibility of glass residues, a corresponding increase in fusibility is expected in formulations of the engobe containing high percentages of glass.

The chemical composition, obtained by XRF, of the two glass residues and commercial frit is presented in **Table 3-3**. Waste glasses display a quite higher content of silica while refractory components, such as aluminium and zirconium oxides, are more abundant in the frit, explaining the greater refractory behaviour of this material, as shown in **Figure 3-33**. Additionally, the presence of fluxing oxides, as Na_2O and K_2O, is slightly more meaningful for the two glass residues, with a total amount of 12.4 and 12.8 wt.% for GM and SP, respectively, and of 9.5 wt.% for the frit. The high percentage of zirconium oxide, 14.2 wt.%, can explain the white colour exhibited by this last material while the green hue displayed by GM glass is probably related to the higher content of iron. On the other hand, the almost total absence of colouring oxides (ZrO_2, ZnO, Fe_2O_3 and TiO_2) justifies the transparency of SP waste.

The loss of ignition value was 1.4 wt.% for glass residues while for the frit was 0.2 wt. %, in accordance with the origin of these materials. In fact, glass residues are waste materials originating from a separation process in recycling plants, while the frit is manufactured starting from pure raw materials.

Table 3-3. Main components of glass residues and commercial frit.

Component	**SiO_2**	**Na_2O**	**CaO**	**Al_2O_3**	**K_2O**	**ZrO_2**	**MgO**	**Fe_2O_3**	**TiO_2**	**Zn**	**LOI**
						(wt.%)					
GM	68.5	11.6	10.7	5.1	0.8	-	1.2	0.34	0.08	0.01	1.4
SP	68.2	12.7	9.7	5.4	0.1	-	2.0	0.03	0.02	-	1.4
Frit	56.4	3.1	9.4	7.3	6.2	14.2	2.3	0.17	0.15	0.34	0.2

In **Table 3-4** are reported the glass transition temperature (T_g), the softening temperature (T_s) and the melting temperature (T_m) of the two glass residues and commercial frit. This latter material shows the highest value for the three parameters while GM provides the lowest T_g and SP and the lowest temperatures for T_s and T_m. Such values are consistent with the observation made for the firing experiment of tablets, as illustrated in **Figure 3-33**. In fact, the lower melting temperatures of GM and SP prove the higher fusibility for these two materials, in comparison to the commercial frit. However, the narrower temperature range between T_s and T_m for GM and SP can imply a lower phase stability for engobes modified using these glass residues.

Table 3-4. Characteristic thermal parameters of glass residues and frit (T_g: glass transition temperature; T_s: softening temperature; T_m: melting temperature).

Material	T_g (°C)	T_s (°C)	T_m (°C)
GM	550	771	1090
SP	600	765	1000
Frit	650	833	1220

3.5.2.2. Rheology of engobe suspensions

In order to prevent any possible drawback occurring during the glazing process of the porcelain stoneware tiles, the rheological behaviour of all the prepared engobe formulations was assessed. Such behavior, described by changes in the viscosity of suspensions as the shear rate increases, is illustrated in **Figure 3-34**. The suspensions with added kaolin (**Figure 3-34 a**) exhibited an increase in initial shear viscosity values up to 3.7 Pa s for 15GM5K sample. In comparison, the standard engobe (Std) registered an initial shear viscosity equal to 0.23 Pa s. However, the increment in viscosity was not proportional to the kaolin content. The samples with 5 wt.% kaolin (15GM5K and 15SP5K) present higher viscosity than those with 10 wt.% (10GM10K and 10SP10K). In both cases, the engobe formulated with GM exhibited higher viscosities than those of the engobe with SP. On the other hand, the addition of only glass waste did not change the viscosity of the suspension relative to the standard, as illustrated in **Figure 3-34 b**. Such result was somehow expected, considering the similar nature of frits and waste glass. It was also expected that the addition of a plastic material as kaolin could have a negative impact on the viscosity of engobe suspensions, especially by inflating values at low shear rates, as suggested by *Lagaly et al.* (Lagaly, 1989). However, the addition of kaolin was resolved in order to reduce the impact of glass residues on the final colour and coefficient of thermal expansion of new engobe formulations (Sanchez *et al.*, 1998; Becker *et al.*, 2017).

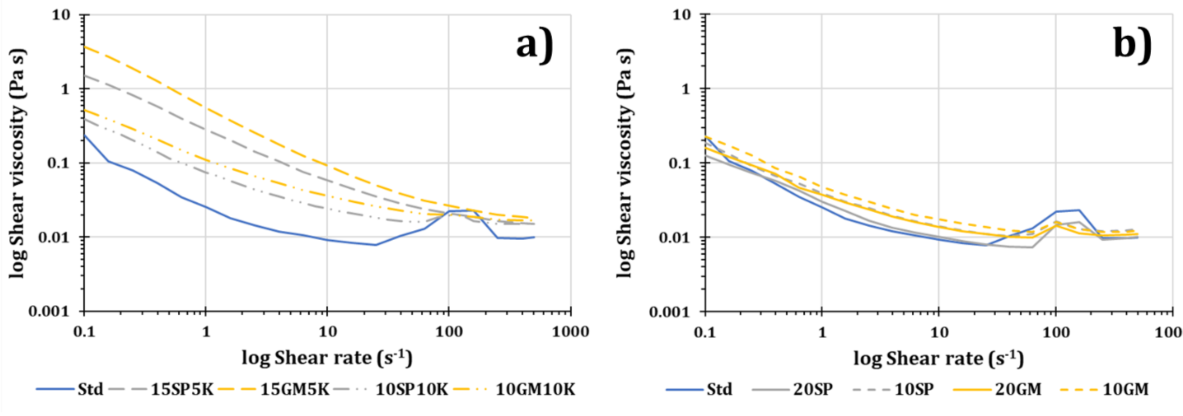


Figure 3-34. Shear viscosity *versus* shear rate for engobe suspensions with a density of 1.45 g/mL. Formulations with **a)** and without **b)** kaolin.

In every case, the viscosity of the slips decreased as the shear rate increased, disclosing a shear thinning behaviour until around 50-100 s^{-1} rates. However, beyond this point, a quick change in the rheological behaviour of the materials was evident for both the standard engobe and all the suspensions without kaolin addition. In fact, the peaks in the last part of the curves correspond to a shear thickening behaviour, where the material displays an increment in viscosity when the shear rate is increased, in this case, until values around 200 s^{-1}, after which the shear thinning is restored. Similar behaviours were found in the literature for glaze slips. It has been suggested by Bergström, 1998, that such events tend to arise earlier when increasing the solid ratio of the suspension and that could be related to the emergence of the hydro-clustering phenomenon. Hydro-clustering occurs when high speed rates operating on solid suspensions encourage the progressive removal of interstitial water between suspended particles, ultimately resulting in agglomeration events that hamper the proper flow of suspension. Even the standard exhibits a shear thickening behaviour in the same identified region. This means that a similar event is not related to the addition of the glass residues and, most importantly, that such phenomenon will not be a problem in the industrial application of the developed waste based engobes.
However, registered values are in accordance with data for ceramic suspension found in the literature (Panya *et al.*, 2005; Fischer *et al.*, 2015). In addition, both this anomaly and the higher viscosity values for suspensions with kaolin can be adjusted through the addition of dispersants and fluidifying agents. This is actually a common practice adopted by manufacturers to adjust the rheology of ceramic suspensions.

3.5.2.3. Characterization of the samples

Thick layers of each sample have been fired at the University of Aveiro in a laboratory muffle at around 1160 °C to pursue a preliminary assessment. The aim was to study the colour (CIEL*a*b* colour coordinates), the sintering behaviour and CTE values of the new engobe formulations in order to select, afterwards, the best promising ones.

In **Table 3-5** the CIEL*a*b* coordinates and coefficient of linear thermal expansion (CTE) values are reported for the whole set of engobe formulations under investigation.

Table 3-5. CIEL*a*b* coordinates and CTE value of thick glaze samples.

Samples	Std	10SP	10SP10K	15SP5K	20SP	10GM	10GM10K	15GM5K	20GM
L*	87.5	87.3	88.8	86.0	85.5	86.2	84.6	83.7	82.7
a*	-0.8	-1	-0.1	-0.8	-0.5	-0.7	-0.1	-0.1	0.2
b*	5.3	5.5	8.7	7.1	7.0	6.6	8.2	8.2	8.9
ΔE	-	0.3	3.7	2.4	2.6	1.8	4.2	4.9	6.1
CTE (10^{-6} K^{-1})	6.63	7.14	7.51	7.84	8.04	7.30	6.84	7.29	7.47

The obtained results show that the substitution of the commercial frit by the SP and GM wastes promotes a decrease of the L* coordinate value. This variation is more pronounced in the samples where total substitution of the frit was applied (samples 20SP and 20GM). The sample with 20 wt.% of GM (20GM) is the one presenting the lowest L* value (82.7). As expected, the addition of kaolin in partial substitution of the frit promoted a slight increase of the obtained L* values. For example, sample 20GM exhibits a L* value of 82.7 and the sample with 10 wt.% of GM and 10 wt.% of kaolin (10GM10K) displays a slightly higher L* value (84.6). The decrease of L* coordinate, for the modified engobes, is probably linked to the reduction of zircon content, as indicated in the work of Dal Bó *et al.*, 2014. These authors found that higher contents of clay and zircon, normally, increase the L* value of ceramic engobes, promoting lighter tones. However, as it can be seen, the benefits granted by the addition of kaolin were not as satisfactory as expected. Indeed, comparing samples 20SP and 20GM with corresponding ones with 10 wt.% of kaolin (10SP10K and 10GM10K), the effect on ΔE value was quite limited, especially for the 10SP10K sample, for which is actually detrimental (higher ΔE value). Again, if comparing 15SP5K to 10SP10K, the addition of kaolin seemed to have played a negative role, as demonstrated by the higher ΔE value of the latter, even if providing a higher L* value. The opposite is though true for 15GM5K and 10GM10K, where kaolin succeeds in decreasing colour differences in the latter formulation, again by increasing the L* coordinate.

As expected, the lowest CTE value is exhibited by the standard engobe while other samples display higher values. The total substitution of commercial frit with waste glass provides engobes with a too high coefficient of thermal expansion to make these formulations substitutes for the commercial engobe under study. In fact, it is known that the frits adopted in ceramic engobes display a coefficient of thermal expansion generally between 6 and 7 x 10^{-6} K^{-1}. Waste glass from panels and containers usually presents values around 9 x 10^{-6} K^{-1} (Navarro, 2003). Likewise, not even the half substitution of the frit by waste glasses can grant CTE values close to the standard, as demonstrated by CTE coefficients of 10SP and 10GM samples, 7.14 x 10^{-6} and 7.30 x 10^{-6} K^{-1}, respectively. On the other hand, the action of kaolin was useful in controlling the

CTE values of the new engobe formulations. The addition of 10 wt.% of kaolin to the engobe formulation promoted a significant decrease of the CTE value. This decrease was particularly evident for the engobe with 10 wt.% of GM and 10 wt.% of kaolin (10GM10K sample), whose CTE is 6.84 x 10^{-6} K^{-1}, a value quite close to that exhibited by the commercial engobe (6.63 x 10^{-6} K^{-1}).

As reported in the literature, the resulting stress within the system glaze-engobe-ceramic substrate are directly proportional to difference in CTE values of layers. However, the extent of such stresses is also related to other factors, such as the Young's modulus of the materials and thickness of layers and, for that reason, there is not an assumed standard limit for the difference of CTE values of glaze and engobe (Taylor and Bull, 1986; Kavanova, 2017). Thus, as mentioned above, among the formulations prepared, the most promising one in terms of CET is the formulation 10GM10K, whose CTE value differs only 3 % with respect to standard engobe.

3.5.2.4. Influence of firing temperature

The two waste glasses under study have a higher fusibility than the commercial frit. Thus, engobe formulations in which the frit was fully replaced by the glasses (20SP and 20GM) can, probably, be fired at a lower temperature without compromising the final properties of the product.

In **Table 3-6** the colour coordinates and colour difference (ΔE) values are reported while in **Figure 3-35** the values of water absorption (a) and shrinkage (b) of samples, in comparison with those of the standard engobe, are presented. The ΔE_1 represents the colour difference of sample 20SP and 20GM calculated by comparing their CIEL*a*b* coordinates with the ones of the standard engobe for each firing temperature, while the ΔE_2 represents the colour difference of samples with respect to the colour coordinates registered for the standard engobe at the industrially firing temperature, 1158 °C. The ΔE_2 values exhibited by samples prepared with the waste transparent glass of solar panels are especially low in the temperature region between 1125-1195 °C, because of the similarity to the colour coordinates of the standard engobe, in particular of L* and a*, representing luminosity and colour range between red and green, respectively. In particular, at the firing temperature of 1125 °C (ΔE_2 = 2.7) the colour difference can be perceived but it is still acceptable On the other hand, if a decrease in industrial firing temperature is assumed, then the adoption of the waste-based engobe 20SP would be even more relevant (ΔE_1 = 2.0) and the colour difference would be perceived only by an experienced observer (Mokrzycki and Tatol, 2011). Conversely, the mix of container glass waste is responsible for the higher values of the b* coordinates, representing the colour range between yellow and blue, and resulting in higher ΔE values for sample 20GM. In this case, the most similar colour is obtained in the range between 1050 and 1108 °C, for both ΔE_1 and ΔE_2 parameters. In particular, the lowest colour difference was registered at 1050 °C where, however, the water absorption and shrinkage values quite differ from the standard.

Table 3-6. Values of the colorimetric coordinates (L*, a*, b*) and colour difference (ΔE) of samples 20SP and 20GM with the firing temperature (T_{max}) relatively to the standard engobe.

Colour coordinates	1050 °C			1078 °C			1108 °C			1125 °C			1158 °C			1195 °C		
	Std	20SP	20GM	Std	20SP	20GM	Std	20SP	20GM	Std	20SP	20GM	Std	20SP	20GM	Std	20SP	20GM
L*	92.1	90.1	89.1	90.9	89.1	87.7	89	87.5	85.1	87	85.5	81.1	87.4	85.8	81.9	89	87.4	84.2
a*	1.92	1.61	1.68	1.8	1.42	1.62	1.26	1.03	1.25	-0.03	0.21	1.34	-0.25	-0.06	0.91	-0.52	-0.37	0.36
b*	7.21	9.61	10.3	7.99	10.1	11.1	8.98	10.6	11.9	8.01	9.29	11	7.46	9.02	10.8	6.82	8.79	10.2
ΔE_1		3.1	4.3		2.8	4.5		2.2	4.8		2	6.8		2.2	6.6		2.5	5.9
ΔE_2	5.2	3.9	3.8	4.1	3.6	4.1	2.7	3.4	5.2	0.7	2.7	7.4		2.2	6.6	1.7	1.3	4.3

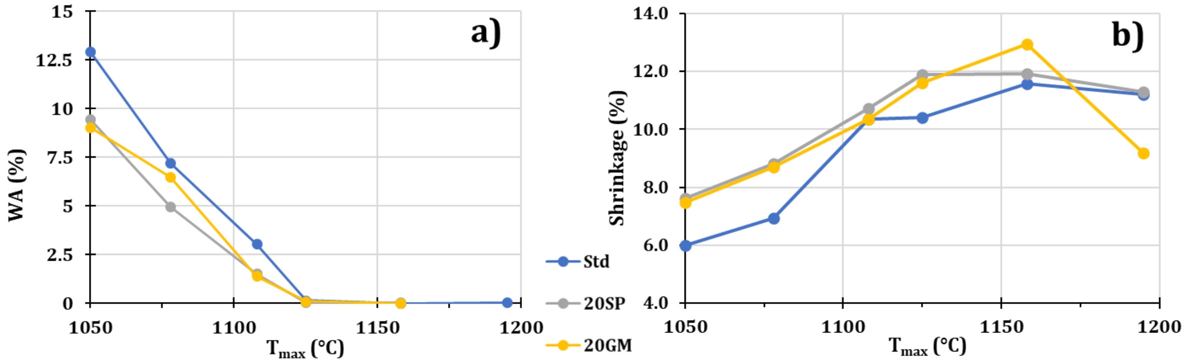


Figure 3-35. Values of water absorption **a)** and shrinkage **b)** of engobe samples, fired at different temperatures (T_{max}).

The water absorption of samples 20SP and 20GM fired at 1195 °C could not be calculated as they were attached to the ceramic support where they were fired. It is clear that the substitution of the frit with waste glass leads to more fusible engobe formulations, which might allow sintering at lower temperatures. The water absorption for 20SP and 20GM is, until 1125 °C, about half of the value exhibited by the standard engobe. For higher temperatures (≥ 1125 °C), the three engobe formulations display zero open porosity. On the other hand, linear shrinkage is higher for both modified mixtures, but for 20SP the trend is very similar to the standard, especially in the temperature range 1108-1195 °C. As observed by Dal Bó *et al.*, 2014 higher linear shrinkage values are displayed for high contents of recycled glass, likely due to the liquid phase formed during firing. The early surge of a liquid phase is also responsible for the reduction of open porosity in engobes, accounting for the reduced water absorption. On this matter, Tarhan & Tarhan, 2020 has suggested as engobes with reduced permeability can help fighting water marks and colour change for ceramic tiles in contact with water.

However, it is not clear how such differences in sintering behaviour could be quantitatively expressed in a lowered firing temperature even if there is plain evidence of a higher fusibility of 20SP and 20GM engobes, compared to standard one. Particularly, sample 20SP seems to possess high phase stability in the region between

1125 and 1158 °C, affording a zero water absorption while not altering the shrinkage. In addition, this sample affords always lower values of water absorption compared to the standard engobe, along the whole set of temperatures.

In order to provide a more exhaustive characterization of the best promising engobe formulations, in **Figure 3-36** the XRD spectra of the standard, 10GM10K and 20SP engobes are represented. It is first noticed as all the spectra confirm the presence of zircon which is, then, present inside the engobe not only through the frit portion. The main crystalline phases are α-quartz, zircon, mullite and albite. In particular, the amount of quartz and mullite in sample 10GM10K seems higher compared to the standard formulation, which might contribute to improve the chemical resistance and hardness of the surface. The increased presence of mullite is probably related to the addition of kaolin. In fact, in sample 20SP, where kaolin was not added, mullite is not present. On the other hand, peaks related to the presence of albite are quite evident, in accordance with the higher amount of sodium oxides inside solar panel glass compared to the frit.

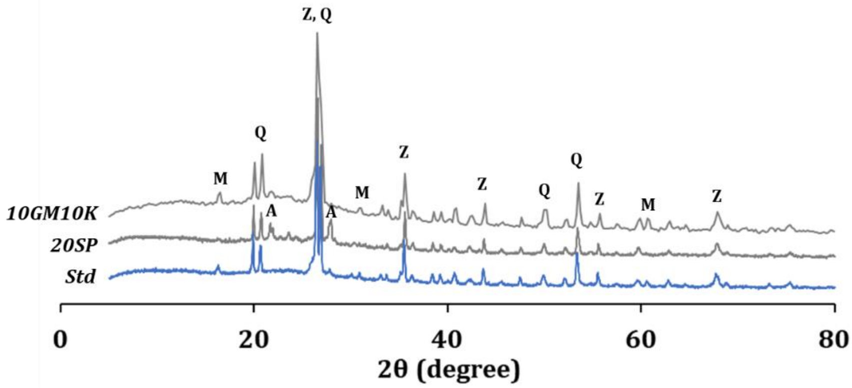


Figure 3-36. XRD spectra of standard engobe (lower) and 10GM10K engobe (upper) with main crystal phases; M: mullite; Q: α-quartz; Z: zircon.

3.5.2.5. Industrial firings

Due to the good results in terms of coefficient of thermal expansion for sample 10GM10K and the promising outcomes for the decrease of firing temperature for sample 20SP, it was decided to run an industrial firing cycle after the deposition of the new waste-based engobes on crude porcelain stoneware tiles by spraying. The commercial transparent glaze was also applied, over the engobe, also by spraying. The firing has been carried out at Aleluia Ceramicas (Aveiro, Portugal) at 1150- 1160 °C (Bullers ring temperature), on a 76 minutes cold-to-cold cycle. The aim was to test the sintering behaviour of the modified engobe during an industrial firing cycle and assess the reactivity of the engobe with the glaze and the ceramic substrate. In fact, reactions can occur at the interfaces of the glaze-engobe-substrate system promoting undesirable effects. As an example, the occurrence of crystallization events can impact over the cooling step, causing cracks and chipping (Peterson *et al.*, 2007; Pradell and Molera, 2020) of the outer layer.

In **Figure 3-37** are illustrated SEM images of the glaze-engobe-ceramic substrate system for standard, 20SP and 10GM10K engobes, together with EDS analysis highlighting the presence of calcium and zirconium.

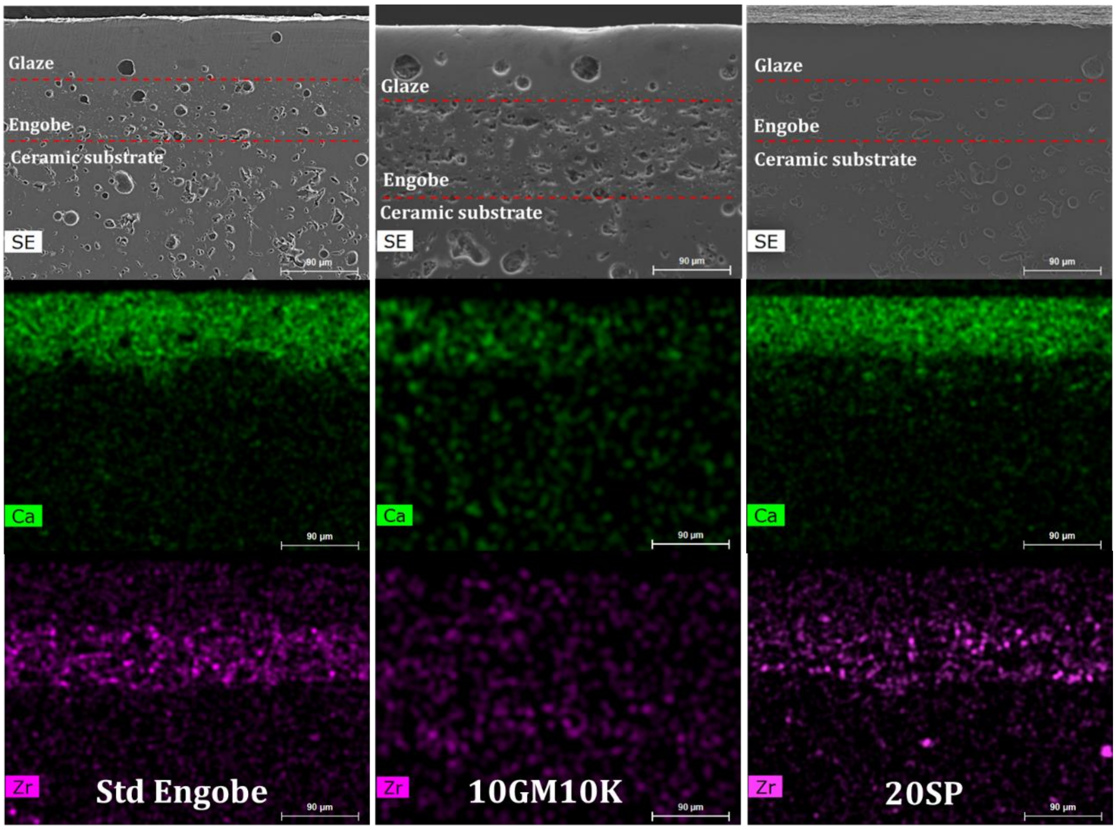


Figure 3-37. SEM and EDS images of surface layers differentiation (ceramic substrate, engobe and glaze layer) for the standard, 10GM10K and 20SP engobes. Calcium is highlighted in green while zirconium in pink.

In all three cases the ceramic substrate exhibits a similar porosity. The engobe layer of 10GM10K shows a similar overall porosity compared to the standard engobe, but the morphology of pores is different being big and round in the standard while smaller and irregularly shaped in the waste-based engobe. In this case, the thickness of the engobe layer is also more pronounced, certainly due to an irregular deposition during spraying. Furthermore, in both standard and 20SP engobes, the glaze layer has almost no pores, while in sample 10GM10K an increased porosity is observed. On the other hand, the engobe layer for 20SP shows fewer pores if compared with the standard sample. This fact can be a further confirmation of the higher fusibility of the engobe containing the solar panel glass. In addition, the EDS images (**Figure 3-37**) highlight that Zr is far more abundant in the standard engobe, granting this commercial formulation a higher opacity and great intensity of white but, as it was demonstrated, a higher melting temperature. In the case of EDS images of 10GM10K sample, it was

not possible to obtain useful information supporting any hypotheses that could explain the behaviour of this engobe. However, the increased porosity in the glaze, together with the shape and number of pores In the engobe layer, suggests as sample 10GM10K can have experience a decrease in fusibility after the addition of kaolin.
In **Table 3-7** are reported the colour coordinates of tiles' surfaces after the industrial firing. It is interesting to see how values, in comparison with those expressed in **Table 3-6**, corresponding to the firing temperature in the same range, changed in an incongruous fashion.

Table 3-7. Values of the colorimetric coordinates (L*, a*, b*) and colour difference (ΔE) of tiles decorated with the standard, 20SP and 10GM10K engobes at 1150-1160°C after industrial firing.

Colour coordinates	1150-1160 °C		
	Std	20SP	10GM10K
L*	85	82.7	86
a*	-0.34	-0.17	-0.83
b*	4.27	5.93	6.86
ΔE		2.8	2.8

In particular, the L* coordinate of the standard and 20SP engobes decreased from 87.4 and 85.8 to 85 and 82.7, respectively, while L* of 10GM10K sample increased from 81.9 to 86, thereby showing the highest lightness value. The a* coordinate underwent to particular changes only in the case of engobe 10GM10K, changing its module from 0.91 to -0.83. All the three engobes displayed a consistent decrease for the b*, going from 7.46, 9.02 and 10.8 to 4.3, 5.9 and 6.9 for standard, 20SP and 10GM10K engobes, respectively. As a final result, the two waste-based engobes performed ΔE values of 2.8 both, where sample 20SP score slightly worst during the industrial firing while sample 10GM10K performed an optimal improvement.

As a consequence of the promising results obtained from the industrial firing test and the appropriate value of the coefficient of thermal expansion, the 10GM10K composition is judged as the most sustainable alternative to the commercial engobe for porcelain stoneware used in this work. On the other hand, the 20SP formulation, because of the promising results obtained from laboratory and industrial firing tests, is proposed as a new eco-friendly engobe to be used in combination with ceramic bodies and glazes characterized by high CTE values. In fact, as a consequence of the poor accordance with the coefficient of thermal expansion displayed by the standard engobe, sample 20SP cannot be adopted as an alternative of the commercial engobe used in the present research work and shall be coupled with materials displaying a similar thermal expansion.

3.5.3. Conclusions

The present work involved the use of two waste glasses as a substitute material for an opaque brilliant zircon frit in a commercial engobe for porcelain stoneware tiles. The main aim was to develop a more sustainable engobe by reducing the amount of costly raw materials (the frit) and using waste glass as a fluxing agent. It was possible to introduce the two waste glasses in the formulation of a commercial engobe without the occurrence of any visible defects and affecting, only slightly, its colour after firing. Besides, such modification did not negatively influence the most sensitive aspects of the process, namely the milling procedure and rheology of the suspensions. In fact, the preparation of suspensions and samples was maintained similar to industrial practice, differing only in the scale but following the same production steps.

In particular:

- Engobe 10GM10K, with a CTE equal to 6.84 10^{-6} K^{-1} and ΔE of 2.8, is proposed as a more sustainable alternative of the commercial engobe. However, further tests investigating possible adverse effects resulting from what appears to be incomplete melting of the engobe layer should be conducted.
- Engobe 20SP, with a CTE equal to 8.04 10^{-6} K^{-1} and ΔE of 2.8, is proposed as a new engobe for porcelain stoneware tiles, to be used in combination with glazes and ceramic bodies with high CTE values. Besides, the high fusibility of solar panel glass provides a relatively low firing temperature, equal to 1125 °C, allowing a lower energy consumption and, consequently, lower CO_2 emissions, compared to the commercial engobes for firing porcelain stoneware tiles.

The good results and the promising tests carried out on commercial tiles at a laboratory scale demonstrated the possibility to use these new engobe formulations as sustainable ceramic materials in the decoration process of porcelain stoneware tiles. In both cases, the reduction of the zircon frit amount can reduce the consumption of synthetic raw materials and, at the same time, avoid the landfilling of relevant amounts of glass waste.

As future development of the present research work, an industrial scale-up can be done in order to point out possible drawbacks arising on a larger scale and to appraise the related economic and environmental impacts on the overall production.

4. Conclusions

4.1. General considerations

In the course of this PhD thesis project, the environmental impact and the sustainability aspects characterizing the Italian ceramic tile sector have been presented and extensively discussed. The main scope was to describe a scenario of the atmospheric emissions and waste management practices from ceramic tile factories located in the Emilia-Romagna region and, especially within the Modena and Reggio-Emilia provinces. The aim, thus, was to provide useful data and instruments for researchers and technicians from the ceramic industry, in order to pave the way for the future sustainable development of this sector, which has proven through the years to be very relevant for the Italian economy and, especially, for the welfare in Emilia-Romagna. However, the high concentration of industrial plants in the *Sassuolo* district, together with the geological configuration of the region and its high population density, pose a serious problem of pollution which, eventually, results in a serious threat for the environment and for the society. Furthermore, the ceramic tile industry involves an extensive use of natural resources, mainly water an minerals and requires high quantity of energy, in particular provided by the combustion of natural gas. All these features certainly constitute serious difficulties that the industry has to face and for which it must somehow take responsibility in order to not let its legitimacy be undermined.

It has been repeatedly noted how much the Italian ceramic tile sector has evolved during the years, and how such evolution interested both the improvement of emission quality by companies and the constant advancement of technological innovation. Regarding this last point, in particular, the great automatization of production processes and the introduction of innovative technologies as, for example, the digital ink-jet decoration or the establishment of the wet route as the main technique for the processing of raw materials, certainly played a fundamental role. On the other hand, the increased concern from both the industrial side and regional institutions, has led to a progressive awareness among manufacturers about the possible hazards related to production processes and, thereby, to great improvements in the safety guidelines and in the adoption of pollution control measures. As consequences, the almost eradication of certain characteristic pollutants (*e.g.*, particulate matter and lead) and the reduction in the number of professional illnesses collected during the last decades can be cited among the most important achievements of the sector (*OPEN DATA INAIL - Quali dati*, 2023).

Furthermore, the improvements in the field of sustainability in this sector are also and above all due to the large number of articles, monographs and collaborative projects collected over the years by the industrial research, represented in the case of the ceramic tile sector by the University of Bologna and the University of Modena and Reggio-Emilia and by research institutes such as *Centro Ceramico*. As has been indicated in the course of this work, and as will be shortly set out in the summary points, the collaboration between institutions and companies is perhaps the decisive factor in guiding the future development of this prosperous industrial sector. In particular, the collaboration between *Centro Ceramico*, the University, the association of ceramic manufacturers *Confindustria Ceramica* and the Emilia-Romagna region has played and continues to play a crucial role in enabling the technological advancement of the sector and in ensuring a high degree of transparency in industrial production, which has proven to be of common benefit to all (**Figure 4-1**).

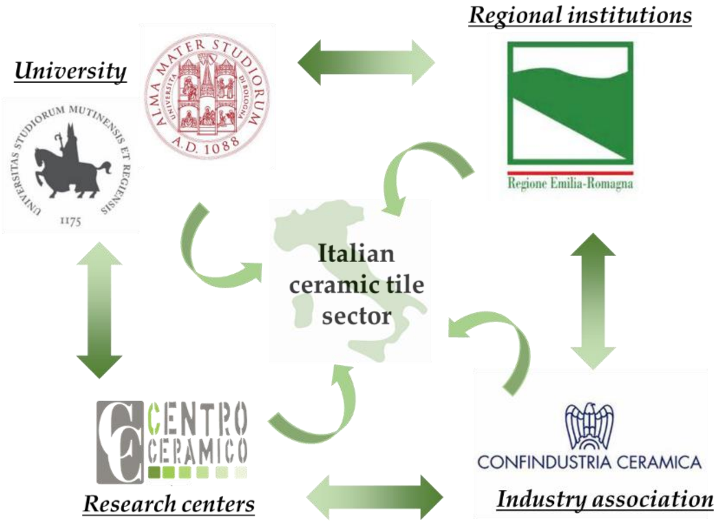


Figure 4-1. main protagonists in the collaboration process for the technological advancement and sustainable development of the Italian ceramic tile sector.

4.2. Summary conclusions

As a result of the present PhD research project, some main conclusions can be drawn and are here disclosed in a more general context. For more detailed information, please refer to the specific conclusions of each experimental chapter. Conclusions are listed as follows:

- Even if the technology involved in the industrial production process of ceramic tiles is basically the same for the greatest portion of the sector, the existence of three different production layouts, here described according to the subdivision in class 1, 2 and 3, results in various differences. Factories belonging to class 1 are characterized by a complete production cycle. In this case, factories are able to recycle their own waste without any particular restraint while in terms of emissions and consumptions, they rank between those belonging to class 2 and 3. It is interesting to notice how this production layout is far the least represented among ceramic tiles factories. On the other hand, far more represented are the classes 2 and 3. The first ones, displaying a complete cycle and producing an excess of spray-dried powder, use to sell this semi-finished product to factories belonging to class 3 which, conversely, display a partial manufacturing cycle but which, often, are simply another industrial installation of the same company. This is especially the case when a big company divide the production of certain specific ceramic tile products in different factories within the territory or simply because of the decision to open a new branch to expand the production, but without investing in an additional raw material processing stage and in another spray-dryer equipment. In this case, however, it has been demonstrated that, in order to facilitate the exchange of both raw materials and waste, factories belonging to class 3 should be located near those of class 2. For the future, such logistic contingency shall be taken into account. In this way, the adoption of transport means can be drastically reduced, facilitating the exchange of resources and reducing also the pollution related to road transport.

- It has been demonstrated that the most characteristic pollutants of ceramic tile manufacturing are particulate matter and fluorine compounds. If not properly contained, these pollutants can represent a serious threat to human health and environmental pollution. However, it has been shown that through the installation of effective filtering devices and the proper management of production processes, these same two pollutants have reached their minimum in the last two decades. The substitution of lead oxide with other chemical species to render good level of brightness in ceramic glazes, on the other hand, has almost eradicated lead as characteristic pollutant related to ceramic tile manufacturing. As a result, the emission factors (g/m^2 or mg/m^2) of particulate matter, fluorine compounds and lead have stabilized to very low values compared to the best available techniques as stated in the Italian regulation (D.M. of 29 January 2007) and according to the most rigorous EU Ecolabel requirements. Other pollutants, as nitrogen and sulfur oxides and volatile organic compounds, including aldehydes, displayed intermittent increasing and decreasing trends over the last eleven years. However, to some extent, a general increase in the emission of the mentioned pollutants can be noticed. Such increase can be explained by reference to recent technological innovations introduced in the ceramic process such as, for example, digital decoration. Furthermore, the concentration values of the mentioned pollutants, reported in **section 3.2**, has demonstrated that their emissions cannot be simply reduced by the increased efficiency of abatement techniques. Conversely, more radical actions shall be implemented as, for example, the adoption of low sulfur-containing clays and inks dispersed in aqueous media and the reduction in the use of sulfur-containing additives.

- Since 2009, the production of ceramic tiles has basically remained constant by ranging in a narrow range between 350-400 mln. m^2. Similarly, the evolution of carbon dioxide emissions, associated with the combustion of natural gas used as the main source of energy within industrial installations, has not changed much. Actually, emissions related to factories belonging to class 1 and 2 even displayed an increasing trend. Such increase has been here tentatively described by referring to the increased thickness of ceramic tiles produced in recent years. However, this consideration must be considered as one of the possible interpretations, also because both large thicknesses and thin thicknesses (< 5 mm) have experienced an increase on the market recently. For these reasons, thus, it remains sometimes hard to link such experimental observations with market trends. Nonetheless, it is important to note here that carbon dioxide is still the main pollutant related to the production of ceramic tiles, being a characteristic byproduct of combustion reactions. Unlike what has been said for the other pollutants characteristic of the process, little can be done to contribute substantially to the reduction of this pollutant. Ceramic technicians certainly focus on the optimal setting of the firing conditions inside kilns and of the working conditions for co-generator or spray-drier equipment, in order to maximize the efficiency related to combustion events. On the other hand, constructors of ceramic equipment constantly aim at the technological advancement of the ceramic processes by improving the energy and material efficiency of their products and trying at the same time to reduce the related emissions of pollutants or, again, by pursuing and evolving new and greener technologies. However, if the goal is to reduce carbon dioxide emissions, only a drastic change by the ceramic tile industry will be effective. In this sense, in order of viability, the reduction of transport means, the implementation of Clean Development Mechanism (CDM) projects, the introduction of carbon sequestration technologies or the progressive electrification of the production process are the only way to face the threat of increasing greenhouse gasses emissions. Still, the ultimate solution of this difficult problem will be the transition toward another energy vector as, for example, hydrogen. It is hard to foretell the feasibility and the convenience of such perspective and, certainly, there is still important research to implement on the field, but it must be pointed out that many companies started looking in that direction and the collected knowledge and expertise on this topic from industrial researchers is each year more consistent.

- It was demonstrated as the recycling of resources is a well-established practice in the Italian ceramic tile sector. Factories producing an excess of spray-dried powder, especially, are able to recycle both water and solid waste up to great extents, even accepting waste materials from other industrial entities. Nonetheless, improving the already high percentages of recycling of resources is fairly achievable at the current level of technology. In fact, the use of glass as substitute for feldspars or the reutilization of both unfired and fired scrap is normally implemented nowadays without any particular technological constraint. However, often the adoption of exotic and highly valuable raw materials is preferred or simply more convenient as a consequence of certain market requirements for white and flawless ceramic bodies or because of the high costs related to the processing and transport of glass and other waste materials. At the light of this situation, industry shall push the public towards more sustainable products by promoting both aesthetic characteristics and environmental benefits of ceramic tiles manufactured after the valorization of resources and not regard aesthetic appearance as the sole leader of the market. Marketing abilities of companies, in fact, can be the game changer for the pursuit of a sustainable development. By promoting greener technologies and recycling practices and by providing the public with the transparent results of LCA studies, companies can increase the demand of greener ceramic products, thereby being able to invest even more in sustainable market choices and further support the technological advancement of the sector.

- The four main generated waste related to the production process of ceramic tiles are unfired and fired scraps, ceramic sludges and exhausted lime. The order in the amount of waste generated is the same for the three different production layouts. In particular, unfired ceramic scrap is the most abundant waste, ranging during the last eight years between 60 and 80 kg/ton for factories belonging to class 1 and 2 and between 40 and 60 kg/ton for factories of class 3. Fired scrap is the second most represented, ranging around 40 kg/ton for class 1 and 2 and around 30 kg/ton for class 3. The generation of ceramic sludges is less constant, but comparable for the three layouts, ranging from a minimum of 20 kg/ton up to a maximum of 60 kg/ton. The same applies for exhausted lime, which production has been varying with fluctuating values around an average of 0.60 kg/ton. All these waste are almost entirely recycled both inside and outside factories, with the only exception of exhausted lime which remains essentially the only waste which is totally landfilled. This is mainly related to its labeling as hazardous waste by the Italian legislation, due to the fact that contains high concentration of fluorine. It is hoped and expected that sooner or later the research will be able to come up with implementable solutions that will ensure exhausted lime recycling without leading to a worsening of the emission profile and rheological properties of ceramic suspensions.

- It is here remarked the decisive role played by sustainability labels on one side and national regulations and international standard one the other. All these tools, in fact, can prove of paramount importance to guide sustainable development. For example, the introduction inside the updated version of the ceramic BREF of new concentration limits for the pollutants related to the most recent technological innovations, as volatile organic compounds and aldehydes, should be adopted at European level, respecting at the same time the boundary conditions and criticalities of each country. Furthermore, the revision of standards and regulations should be harmonized to some extent, using similar impact assessment criteria and adopting identical units of measurement, thus facilitating and speeding up the processes of compliance with the different guidelines. Finally, it is reminded how it is important to set specific emission limits and performance standards but how delicate can be at the same time the choice for the quantitative values for such specifications. It is not simply by setting ever more rigorous environmental standards that sustainability can be bolstered. In fact, regulations and labels shall stand for environmental protection and sustainable development but supporting economic growth by promoting competitiveness among companies rather than by setting insurmountable barriers to company business.

- It was deemed necessary to make a point about borderline aspects that are sometimes overlooked or, on the contrary, overestimated. Certain technological solutions and circular economy policies are often advocate outside of the context of each specific industrial reality. In the case of the ceramic tile sector, the pursuit of a *closed-loop* recycling for waste materials rather than of *open-loop* perspectives, the adoption of post-combustors or co-generator equipment and the choice for specific configuration of the product, as ventilated façades or big thicknesses or the color and texture of the ceramic surfaces, are some of the examples where convenience in terms of sustainability has to be defined for each specific solution in a broad context. No simple environmental advantage can be set forth as inherent characteristic for the mentioned solutions. As an example, the *closed-loop* view is often deemed as the preferable choice for waste recycling, but it can actually happen that another industrial sector can beneficiate better through the exploitation of certain waste rather than its own. Post-combustors are responsible of higher levels of carbon dioxide emissions, but their implementation can be beneficial in certain cases where the release of hazardous volatile organic compounds is associated with a severe risk for the human health. Again, the choice for a higher thickness of ceramic tiles can be related to a higher consumption of raw materials and higher emissions from spray-driers but can contribute to extend the lifespan of those surfaces subjected to particular stresses that, otherwise, would require additional maintenance with a corresponding consumption of resources. It is not easy to foretell the consequences for the adoption of certain technologies or for the pursuit of particular resource management policies in the long run. It is mainly for this reason that it was decided to highlight these aspects and to emphasize the importance of LCA and viability studies as essential tools to guide sustainable development in each specific context.

- An experimental contribution to waste recycling where two glass residues were used in the development of a ceramic engobe for porcelain stoneware tiles was presented. In this work, two sources of glass were adopted as substitutes for a white zircon frit contained at 20% inside a commercial engobe formulation. The aim was to develop a more sustainable engobe by reducing the amount of costly raw materials and using waste glass as a fluxing agent. Rather than at the development of the best performing solution, the experiments focused on the technical performance of some principal formulations with respect to some key features of the ceramic tile manufacturing process as the milling step, the rheology of engobe suspensions, the colorimetric characteristics and thermal expansion of engobes and their sintering behavior. In fact, it was noted that the already sparse literature on the use of glass in ceramic engobes completely lacks examples of applications on industrial and semi-industrial scales. For this reason, the experiments were conducted with the aim of highlighting possible drawbacks arising from a possible future industrial application and performing an industrial firing on porcelain stoneware tiles decorated with the studied engobes. Two waste-based ceramic engobes were proposed. Sample 10GM10K was proposed as a more sustainable alternative of the commercial engobe. However, further tests investigating possible adverse effects resulting from what appears to be incomplete melting of the engobe layer should be conducted. Sample 20SP was proposed as new engobe for porcelain stoneware tiles, to be used in combination with glazes and ceramic bodies characterized by high CTE values. Future research on this topic will focus on improving the technical characteristics of the proposed engobes. In this way, it will be possible to take a step further toward the industrial implementation of these waste-based engobes, thus contributing to the reduction of raw material use and energy consumption for the production of synthetic frits and, at the same time, saving from landfills significant amounts of glass waste.

4.3. Conclusive remarks

The data reported in the present PhD research project, together with the experimental work and the detailed description of the production process of ceramic tiles constitute a comprehensive collection of important information which can result of crucial relevance for the future development of this industrial sector. For this reason, it is deemed as imperative responsibility for the Italian ceramic tile industry to continue supporting and encouraging the scientific research on issues of sustainability and technological advancement.

It has been proven how sustainability is not a simple concept, certainly not a certain science, and, ultimately, how it is a rough path to follow. Nonetheless, the introduction of sustainability concepts and of sustainability itself seemed to be having promoted along the years the collaboration between different fields of knowledge for the resolution of problems. Therefore, complex problems as climate change, world hunger, human exploitation, flora and fauna conservation and other deep-rooted questions that pose into danger an ever more complex human ecosystem represented by the environment, the society and economy will not simply be solved by addressing solely science or, on the contrary, relying exclusively on politics or economy. In this context, sustainability has become the pole star in the development of society and human sciences, the meeting point between chemistry and economics, physics and sociology, politics and geology, the place of comparison and improvement for different expertise and, hopefully in the near future, a model for people's behavior.

For that reason, this PhD research project sought to assess the environmental impact and sustainability of the Italian ceramic tile industry in an exhaustive manner, trying to provide the reader with a comprehensive view of this important industrial sector. In this way, having experience of the ceramic tile industry's past and present state of the art, the road to its future sustainable development will be certainly brighter.

Annex I

Development of a new method for the assessment of scratch resistance of ceramic tiles

I. Introduction

In this annex is reported the experimental work carried out on a sample of different ceramic tiles with the aim of developing a new test method to measure the scratch resistance of ceramic tiles, so as to provide a more rigorous alternative to the Mohs method.

Scratch resistance is one of the technical features of materials used to describe their hardness. It is easy understandable the importance of hardness for covering materials in building applications, where tiles can often be subjected to great stresses. For example, floors in areas characterized by high flows of people, such as supermarkets or airports, should possess high hardness, while wall tiles or tiles in home areas subject to low stress can certainly have lower hardness values. Hard tiles can better withstand scratches and hurts without being damaged, with a double benefit. In fact, a damaged ceramic surface leads not only to aesthetic damage but also to greater difficulty in cleaning, as holes and scratches can collect dirt that, as a result, becomes difficult to remove.

There is another fashion in which the hardness of surfaces can be expressed, that is, the indention hardness. There are numerous test methods for determining this feature of materials, the major ones being the Knoop's, Brinell's, Vickers's, Rockwell's and Shore's hardness tests, all of which are internationally standardized (ISO 4545-1:2017, 6506-1:2014, 6507-1:2018, 6508-1:2015, 7619:2010). Each method will be most suitable for a distinct class of materials or for specific surface conditions. However, most of the standardized methods relate to applications for metals or elastomers. For ceramic materials, on the other hand, the hardness of surfaces is assessed by measuring the resistance to scratch and, especially, by referring to the international standard BS EN ISO 20502:2016 "Fine Ceramics (advanced ceramics, advanced technical ceramics) – Determination of adhesion of ceramic coatings by scratch testing" (*BS EN ISO 20502:2016*). The testing method involves scratching a few mm into the surface of the specimen using an indenter with a specific geometry (Rockwell, in accordance with the standard ISO 6508-1:2015). The scratch is then observed under a microscope, assessing the damage to the surface. The result is expressed in a graph where the different damage events (Lc_1, Lc_2 etc.) are expressed as a function of the various parameters recorded by the instrumentation. Even though this standard provides a rigorous methodology for the determination of the hardness of ceramics it is rather addressed to advanced ceramic materials, as actually defined in the title. Until 2008, the standard EN 101:1991 "Ceramic tiles – Determination of scratch hardness of surface according to Mohs" defined the testing method for the assessment of scratch hardness of tiles by addressing the Mohs hardness scale. Thus, a simple, fast and reliable method to determine this feature of ceramic tiles is currently lacking.

In fact, it has been realized that a simple updating of the mentioned standard is not desirable because of the numerous drawbacks that both the test method and the Mohs scale itself display. Specifically, the scale is based on the qualitative difference in the hardness of some common minerals and goes from 1 to 10 expressing hardness in integer values and being 10 the upper limit. However, such classification is a merely qualitative appraisal of the hardness of materials which does not possess a solid scientific base. As illustrated in **Figure A-I**, in fact, the levels of the Mohs scale does not provide a faithful and quantitative description of the actual hardness of materials as, on the other hand, other methods do.

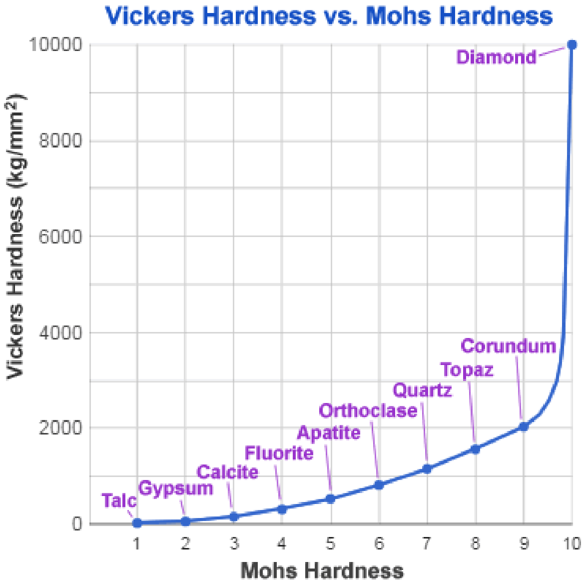


Figure A-I. The values from the Vickers hardness method form a continuous scale which provides more information about the hardness of materials when compared to the levels of the Mohs scale (*Mohs Hardness Scale: Testing the Resistance to Being Scratched*, 2022).

The old testing method is also not without flaws. It involves etching the test surface with some specific sharp-edged minerals characterized by increasing hardness until a scratch is left on the surface of the material being tested. The hardness value assigned to the specimen is equal to the level of the Mohs mineral that has marked the scratch. Obviously, this approach is particularly sensitive to various factors as, for example, the strength of the operator and the geometry of the scratching edge. Furthermore, even the determination of the scratch can be problematic, being also subject to the subjectivity of the operator. A different rating may be given based on surface color, texture or because of eyesight conditions or simply because of meters of personal judgment. It is in fact clear how a scratch is normally more appreciable on a smooth black surface rather than on a rough white one.

Different expedients have been devised in order to overcome some of the mentioned issues. One particular alternative to the adoption of the Mohs' reference minerals for testing are the so called "hardness picks", illustrated in **Figure A-II**.

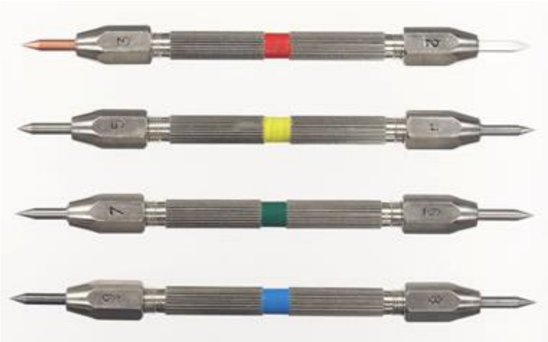


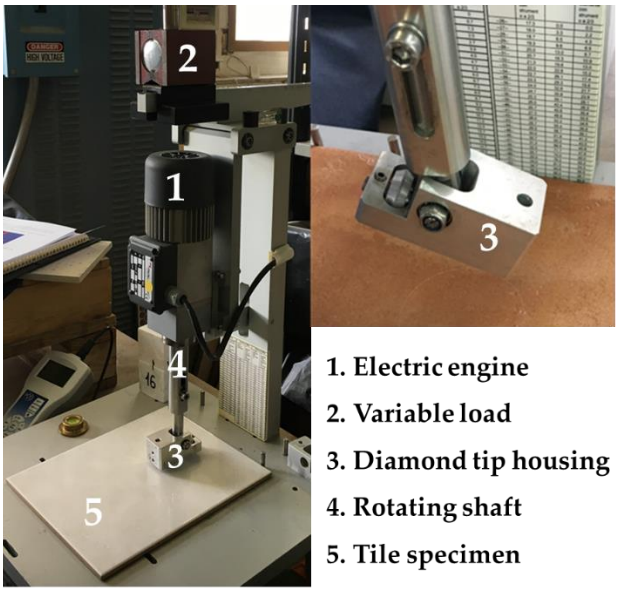
Figure A-II. Hardness picks with their metal stylus and the alloy pick, marked with the increasing values of the Mohs hardness scale (*Mohs Hardness Scale: Testing the Resistance to Being Scratched*, 2022).

These picks have sharp points made up of specific metals and alloys that can be used for a more accurate testing. The picks can easily be sharpened and allow a finer degree of control, allowing to test particularly small sample and avoiding the high variability related to the nature of the scratching edge in the classic method. However, the dependance on the operator strength is still an issue for result variability. Further, the mentioned issues related to the scratch assessment method remain. The inherent difficulty in the evaluation of the scratch is also related to the fact that ceramic is a composite material, consisting of different crystalline phases each with its own hardness and embedded in a glassy matrix characterized by a further different hardness. Furthermore, the presence of open porosity and the possible occurrence of particular structures and rough textures on the surface of tiles makes even more difficult to obtain repeatable results. On the other hand, however, it is true that a quick and practical testing method for a product such as ceramic tile cannot involve the use of sophisticated instrumentation that produces complex results and involves expensive analysis.

An important activity that has been implemented during this PhD research project was the development of an alternative testing to the Mohs method for the evaluation of scratch resistance for ceramic tiles. In particular, the focus was put on attempting to eliminate variability due to operator subjectivity during scratch performance.

II. Materials and methods

The execution of the scratch on the surface of ceramic tiles has been performed with the instrument represented in **Figure A-III**.



1. **Electric engine**
2. **Variable load**
3. **Diamond tip housing**
4. **Rotating shaft**
5. **Tile specimen**

Figure A-III. Scratch tester designed by *Centro Ceramico* with numerated construction constituents.

The instrument was designed and built by professionals from *Centro Ceramico* and consists in a rotating shaft with attached to the lower end a self-adjustable housing for a diamond tip, capable of engraving circles on the surface of the test tiles and adapting to the surface and thickness of the specimen due to movable joints. An increasing load can be added on top to increase the resulting pression on the diamond tip and, thereby, the force applied to the scratching.

The sample of ceramic tiles on which the tests were conducted consisted of 14 tiles, supplied by different companies and presenting different characteristics such as the nature of the ceramic body, surface texture and color shade (**Table A-I**).

Table A-I. Characteristics of the tiles sample, according to nature of the ceramic body, surface texture and surface mechanical treatment and color shade.

Ceramic body	Surface texture	Surface treatment	Color shade
13 porcelain stoneware (PS) **1** red monoporosa (RM)	**10** smooth (S) **3** textured (T) **8** rough (R)	**10** unpolished (UP) **4** polished (P)	**5** dark (D) **8** light (L) **2** grey (G)

The sample is representative of the actual market of ceramic tiles, characterized mainly by cool tones and decorative patterns recalling for natural stones. Each tile characteristic was assigned with a label for easy visualization of results.
The operating conditions of the instrument have been maintained as follows:

- Diamond tip rotating speed: 1 rpm.
- Diamond tip geometries: conical base pyramidal tip and square base pyramidal tip.
- Tip angle: 90°.
- Applied loads: 0.05, 0.1, 0.2, 0.4, 0.7, 1.0, 1.4 kg.

On the other hand, the evaluation of the scratch was performed under the following conditions:

- Powder removal: with a 10% HCl solution and after removing the excess acid with a damp cloth.
- Scratch evaluation: carried out by the operator under 300 lumen of light and from a distance of 30 cm at different angulations.

The same testing procedure has been also carried out with two other different diamond tips with angles of 60° and 120°. However, in the first case the tip resulted too sensitive and fragile and after some test at even low loads broke. In the second case, instead, the tip resulted poorly sensitive to load changes and a proper subdivision of the scale could not be realized. For this reason, a diamond tip with an intermediate angle (90°) was chosen as the best choice that would have minimized the mentioned drawbacks.
A new scale for the representation of results was designed by identifying seven specific load and by dividing the step according to eight different "hardness classes", as reported in **Table A-II**. Results were expressed by assigning the hardness class corresponding to the first load capable of scratching a circle evaluated for 100% of the circumference visible by the operator.

Table A-II. New designed hardness scale with variable loads and corresponding hardness classes.

Load	**> 1.4 kg**	**1.4 kg**	**1.0 kg**	**0.7 kg**	**0.4 kg**	**0.2 kg**	**0.1 kg**	**0.05 kg**
Hardness class	A+	A	B	C	D	E	F	G

III. Results and discussion

The results of the first set of tests, performed by using a conical base pyramidal tip are reported in **Table A-III**, while **Table A-IV** accounts for the second set of tests, performed by using a square base pyramidal tip.

Table A-III. Description (in order, according to ceramic body type, surface texture, surface treatment and color shade), scoring and hardness class assignment of the sample scratch with a conical base pyramid tip.

Sample	Description	0.05 kg	0.1 kg	0.2 kg	0.4 kg	0.7 kg	1.0 kg	1.4 kg	Hardness class
T1	PS-R-UP-D	🟩	🟩	🟩	🟩	🟥	🟥	🟥	D
T2	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T3	PS-T-UP-G	🟥	🟥	🟥	🟥	🟥	🟥	🟥	A+
T4	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T5	PS-R-UP-D	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T6	PS-R-UP-D	🟩	🟩	🟩	🟩	🟥	🟥	🟥	D
T7	RM-S-UP-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T8	PS-T-UP-D	🟩	🟩	🟥	🟥	🟥	🟥	🟥	B
T9	PS-T-UP-L	🟩	🟩	🟩	🟥	🟥	🟥	🟥	C
T10	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T11	PS-S-UP-G	🟥	🟥	🟥	🟥	🟥	🟥	🟥	A+
T12	PS-S-UP-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T13	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T14	PS-S-UP-D	🟩	🟩	🟩	🟥	🟥	🟥	🟥	C

Table A-IV. Description (in order, according to ceramic body type, surface texture, surface treatment and color shade), scoring and hardness class assignment of the sample scratch with a square base pyramid tip.

Sample	Description	0.05 kg	0.1 kg	0.2 kg	0.4 kg	0.7 kg	1.0 kg	1.4 kg	Hardness class
T1	PS-R-UP-D	🟩	🟩	🟩	🟩	🟥	🟥	🟥	D
T2	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T3	PS-T-UP-G	🟥	🟥	🟥	🟥	🟥	🟥	🟥	A+
T4	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T5	PS-R-UP-D	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T6	PS-R-UP-D	🟩	🟩	🟩	🟩	🟥	🟥	🟥	D
T7	RM-S-UP-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T8	PS-T-UP-D	🟩	🟩	🟥	🟥	🟥	🟥	🟥	B
T9	PS-T-UP-L	🟩	🟩	🟩	🟩	🟩	🟥	🟥	E
T10	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T11	PS-S-UP-G	🟩	🟥	🟥	🟥	🟥	🟥	🟥	A
T12	PS-S-UP-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T13	PS-S-P-L	🟩	🟩	🟩	🟩	🟩	🟩	🟩	G
T14	PS-S-UP-D	🟩	🟩	🟩	🟩	🟥	🟥	🟥	D

Results are quite consistent. In particular it is soon noticed how all polished (P) surfaces are always scratched at the minimum load. This fact can be explained by considering that the polishing treatment, despite being able to flatten the surface and increasing its smoothness and shine, contributes also to an increase in the open porosity, in fact providing the tip with more niches to make the first incision. After that, once the surface is nicked, the scratch can easily proceed along the entire length of the circumference.

Differences in results attributable to color shades of tiles were not observed. Both dark (D) and light (L) tiles are equally scratched. However, it should be noted how this result is due to the process of cleaning the surface with the 10% HCl solution, necessary to remove the dust. In fact, if this step is avoided the black surfaces score significantly lower because of the higher reflectance of dust on the black background. Another feature displaying no influence on the assignment of the hardness class seems to be the nature of the ceramic body under the glaze layer, being porcelain stoneware (PS) tiles equally scratched as the red monoporosa (RM) specimen. On the contrary, what actually seems to be relevant is the occurrence of some textures (T) on the surface. This can be explained by the fact that usually textured tiles are left unglazed, displaying the porcelain stoneware body characterized by high hardness.

Nonetheless, minor differences in the score and, thus, in the assignment of the hardness class have been registered. In particular, sample T9 and T 14 were assigned with an inferior hardness class in the case of the tests performed with a square base conical tip, suggesting that the geometry of the tip is important. In fact, after the inspection of the two diamond tips under an optical microscope (**Figure A-IV**), it was discovered that the square base tip had detected some damage, likely contributing to the differences mentioned.

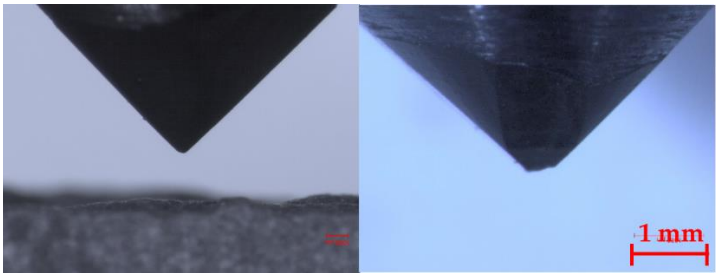


Figure A-IV. Magnification of the conical-based pyramidal point (left), intact, and the square-based pyramidal point (right), damaged.

The conical base tip, otherwise, was continuously checked for the occurrence of further damage events that, eventually, did not occur at least up to 100 scratching tests. To rigorously evaluate the role of tip geometry, that is, whether it can really contribute to some difference in results or whether, as in this case, it is exclusively more sensitive to breakage, experimentation should continue, and tests should be repeated. However, this fact suggests that the evaluation of the integrity of the scratch medium shall be included as a mandatory step in the testing method in order to guarantee a better reproducibility of results. Thanks to another set of experiments which is not reported here, it was also possible to demonstrate that at higher rotating speed, in particular at 2 rpm, the tip undergoes breakage more easily, especially with textured surfaces as the one reported on the left in **Figure A-IV**.

In order to assess the quality of the method proposed here, a comparison of the results obtained with the conic base pyramidal tip according to the present classification with those obtained by carrying out the Mohs test with the minerals and hardness picks is presented in **Table A-V**.

Table A-V. Correlation between classification methods for the assessment of the scratch hardness of ceramic tiles, according to Mohs scale, with both hardness picks and minerals, and the hardness class designed in the present work (conic base pyramidal tip).

Sample	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14
Mohs scale Hardness picks	6	4	7	6	5	7	5	8	7	5	7	4	6	7
Mohs scale Minerals	5	4	9	5	4	7	4	7	7	4	8	4	5	8
Hardness class	D	G	A+	G	G	D	G	B	C	G	A+	G	G	C

It is first noted that the method providing the widest classification range is the assignment of a hardness class according to the new proposed method. In fact, in this case, assigned classes go from D to A+, encompassing all the eight levels of the scale. On the other hand, the classification according to the Mohs scale involve the assignment of only six classes, from level 4 to 9. This suggests that the proposed scale is more suited for the specific aim of evaluating the hardness of a certain class of materials, in this case of ceramic tiles, where the Mohs scale is on the contrary applicable to theoretically all existing solid materials and, for that reason, less convenient for the present scope. Furthermore, the inconsistency in the data displayed by the use of the hardness picks and minerals indicates the test result to be largely dependent on various factors, including the geometry of the scratcher edge and, probably, the strength of the operator, which cannot have been the same in drawing a mineral on the ceramic surface or, conversely, a pencil with a comfortable grip.

The observation of the scratch by a human operator under certain light conditions was considered the best assessment method for the purpose of this test. However, other experiments were carried out with the aim of providing an additional method of assessment that could be at the same time more objective and rigorous. Unfortunately, the observation of the scratch with an optical microscope, in addition to lengthening the testing time, did not provide any advantage of objectivity in damage assessment. Indeed, it was found that scratches that were not visible to the naked eye still remained undetectable under the microscope, while ambiguous scratches remained difficult to assess even through the use of sophisticated instrumentation. Neither the evaluation through the profilometer was able to discriminate the damage and provide useful information, making simple visual evaluation the easiest, fastest and most economical and coherent method for the evaluation of scratches.

IV. Conclusions

During this work, a new testing method for the evaluation of the scratch resistance of ceramic tiles was proposed as alternative to the Mohs test. This method, in fact, presents various drawbacks, especially in the performance of the scratch and in the classification of results. The Mohs scale is based on a simple qualitative appraisal of the hardness of some common minerals and the level of the scale are actually not proportionally separated. Furthermore, the outcome of the test depends extremely to the integrity and shape of the mineral's edge scratching the ceramic surface. It was tried to solve this drawback by introducing the so-called hardness picks to provide a more comfortable grip and always sharpen tips performing the scratches. However, even this method is not exempt from the subjectivity of the operator, particularly the strength the scratch is performed with, which is difficult to control.

In the proposed method, a new instrument designed by *Centro Ceramico* was used to carry out scratching test with increasing loads, trying to eliminate the contribution of the operator. After the testing and the evaluation of results, the following conclusions can be drawn:

- The geometry of the tip is important but not fundamental. What is actually fundamental is the integrity of the tip during the testing. For this reason, the scratcher must possess a tip made out of diamond and rotate at low rates (for example, 1 rpm) and the integrity of the tip must be checked for damage after a chosen number of scratches. Higher rotating speed (2 rpm) can lead to the breakage of the tip, especially with textured surfaces.
- The classification of results, in this case performed assigning a particular "hardness class", should be designed with the specific aim of discriminating the scratch resistance of ceramic tiles on the whole span of the scale. The suggested scale displays eight level of hardness, from G to A+, each one corresponding to a specific load (from 0.05 to 1.4 kg) and, thereby, to a specific force applied on the tip.
- Another fundamental part of the testing method is the cleaning procedure of the surface. In this case, a 10% HCl solution followed by a rinse with water was used to remove the ceramic powder that can alter the results by disfavoring dark shades.

- All polished (P) surfaces were always scratched at the minimum load. This fact can be explained by considering that the polishing treatment contributes to increase the open porosity on the tile's surface, providing the tip with more niches to make the first incision and to proceed in the scratch more easily. Furthermore, textures (T) surfaces, among unglazed tiles, were assigned with the high hardness values. In fact, the three textured tiles of the sample scored two of the three highest assigned hardness classes (A+ and B)
- The visual evaluation method, although not free from operator subjectivity, is proposed to be the best scratch evaluation method because it is faster, more practical and less expensive than other methods involving analytic instrumentation. What is important, is to set standardized illumination and observation conditions, so as not to provide additional chance for variability.

The performed experiments and the collected results provided a great number of precious information which allowed to draw some important conclusions on the strengths of this method and, at the same time, to highlight its weaknesses. However, the observation of these latter, served the chance to propose further developments of the present research in order to design a successful method for the evaluation of the scratch hardness of ceramic tiles. In particular, future research shall be aimed at:

- Defining the conditions for checking the integrity status of the diamond tip. In fact, how it was possible to see, differences in the geometry of the scratching edge can lead to flawed results.
- Expanding the sample of ceramic tiles, with a focus on various kinds of glaze and on the difference between glazed and unglazed tiles. In fact, it was demonstrated that the nature of the glaze was fundamental in the assignment of the hardness class. Probably it will be necessary to differentiate between glazed and unglazed tiles and provide two different scales and/or variations in the testing method.
- Providing additional data on the reliability of the visual evaluation for the scratch assessment, for example by showing divergences in the assignment of the hardness class by different operators.

The proposed alternative method to the Mohs test shall certainly be refined for consistency purposes. Nevertheless, it was possible to overcome the drawbacks of the old method related to the geometry of the scratcher and the strength applied by the operator. By proceeding along with the experimentation according to the suggested points, it will be possible to design a testing method for evaluating the scratch resistance of ceramic tiles which can be practical and fast and, at the same time, dependent on as few variables as possible.

References

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) (2000) OJ L. Available at: http://data.europa.eu/eli/dec/2000/532/oj/eng (Accessed: 14 October 2022).

2009/607/EC: Commission Decision of 9 July 2009 establishing the ecological criteria for the award of the Community eco-label to hard coverings (Notified under document C(2009) 5613) (Text with EEA relevance) (2009) OJ L. Available at: http://data.europa.eu/eli/dec/2009/607/oj/eng (Accessed: 6 October 2022).

‘A look at ways of controlling tailings to avoid future liability’ (2022) Canadian Mining Journal. Available at: https://www.canadianminingjournal.com/featured-article/a-look-at-ways-of-controlling-tailings-to-avoid-future-liability/ (Accessed: 7 October 2022).

Abdrakhimov, V.Z., Togzhanov, I.A. and Saibulatov, S.Zh. (1990) ‘Waste materials from nonferrous metallurgy in ceramic bodies’, Glass and Ceramics, 47(8), pp. 287–290. Available at: https://doi.org/10.1007/BF00677954.

Acimac and Mecs (2022) World production and consumption of ceramic tiles. 10th. Available at: https://www.acimac.it/area/centro-studi/documentazione/#servizi.

‘Advancing Sustainable Materials Management: 2018 Tables and Figures’ (2020), p. 84.

Ahmaruzzaman, M. (2010) ‘A review on the utilization of fly ash’, Progress in Energy and Combustion Science, 36(3), pp. 327–363. Available at: https://doi.org/10.1016/j.pecs.2009.11.003.

Amorós, J.L. et al. (2007) ‘Effect of the green porous texture on porcelain tile properties’, Journal of the European Ceramic Society, 27(5), pp. 2295–2301. Available at: https://doi.org/10.1016/j.jeurceramsoc.2006.07.005.

Anderson, R.S. and Anderson, S.P. (2010) Geomorphology: The Mechanics and Chemistry of Landscapes. Cambridge University Press.

Andji, J.Y.Y. et al. (2009) ‘Iron role on mechanical properties of ceramics with clays from Ivory Coast’, Ceramics International, 35(2), pp. 571–577. Available at: https://doi.org/10.1016/j.ceramint.2008.01.007.

Andreola, F. et al. (2006) ‘Recycling of the Waste Waters Into Porcelainized Stoneware Ceramic Tiles: Effect on the Rheological, Thermal and Aesthetical Properties’, in Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VII. John Wiley & Sons, Ltd, pp. 21–29. Available at: https://doi.org/10.1002/9781118371435.ch3.

Andreola, F. et al. (2007) ‘CRT glass state of the art: A case study: Recycling in ceramic glazes’, Journal of the European Ceramic Society, 27(2), pp. 1623–1629. Available at: https://doi.org/10.1016/j.jeurceramsoc.2006.05.009.

Andreola, F. et al. (2008) ‘Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production’, Ceramics International, 34(5), pp. 1289–1295. Available at: https://doi.org/10.1016/j.ceramint.2007.03.013.

Barrachina, E. et al. (2017) ‘Ceramic porcelain stoneware production with Spanish clays purified by means of the removal of iron compounds and organic matter using physical methods’, Applied Clay Science, 143, pp. 258–264. Available at: https://doi.org/10.1016/j.clay.2017.03.024.

Becker, E. et al. (2017) 'Use of mechanically-activated kaolin to replace ball clay in engobe for a ceramic tile', Ceramica, 63, pp. 295–302. Available at: https://doi.org/10.1590/0366-69132017633672077.

Bellotto, M. et al. (1995) 'Kinetic study of the kaolinite-mullite reaction sequence. Part I: Kaolinite dehydroxylation', Physics and Chemistry of Minerals, 22(4), pp. 207–217. Available at: https://doi.org/10.1007/BF00202253.

Bergström, L. (1998) 'Shear thinning and shear thickening of concentrated ceramic suspensions', Colloids and Surfaces A: Physicochemical and Engineering Aspects, 133(1), pp. 151–155. Available at: https://doi.org/10.1016/S0927-7757(97)00133-7.

Bernardo, E. (2008) 'Fast sinter-crystallization of a glass from waste materials', Journal of Non-Crystalline Solids, 354(29), pp. 3486–3490. Available at: https://doi.org/10.1016/j.jnoncrysol.2008.03.021.

Berrone, P., Fosfuri, A. and Gelabert, L. (2017) 'Does Greenwashing Pay Off? Understanding the Relationship Between Environmental Actions and Environmental Legitimacy', Journal of Business Ethics, 144(2), pp. 363–379. Available at: https://doi.org/10.1007/s10551-015-2816-9.

Bethke, C.M., Vergo, N. and Altaner, S.P. (1986) 'Pathways of Smectite Illitization', Clays and Clay Minerals, 34(2), pp. 125–135. Available at: https://doi.org/10.1346/CCMN.1986.0340203.

Biasini, V. et al. (2003) 'Effect of talc and chlorite on sintering and technological behaviour of porcelain stoneware tiles', p. 15.

Böhm, S., Misoczky, M.C. and Moog, S. (2012) 'Greening Capitalism? A Marxist Critique of Carbon Markets', Organization Studies, 33(11), pp. 1617–1638. Available at: https://doi.org/10.1177/0170840612463326.

Bondioli, F. et al. (2010) 'Characterization of Rice Husk Ash and Its Recycling as Quartz Substitute for the Production of Ceramic Glazes', Journal of the American Ceramic Society, 93(1), pp. 121–126. Available at: https://doi.org/10.1111/j.1551-2916.2009.03337.x.

Bonvicini, G., Fregni, A. and Palmonari, C. (2006) 'Chapter 7: Fluorine Compounds in Gaseous Emissions from Industrial Sources: The Case of Ceramic Industries', in A. Tressaud (ed.) Advances in Fluorine Science. Elsevier (Fluorine and the Environment), pp. 225–249. Available at: https://doi.org/10.1016/S1872-0358(06)01007-4.

Boschi, G. et al. (2020) 'Sustainability in Italian Ceramic Tile Production: Evaluation of the Environmental Impact', Applied Sciences, 10, p. 9063. Available at: https://doi.org/10.3390/app10249063.

BREEAM | BRE Group (2022). Available at: https://bregroup.com/products/breeam/ (Accessed: 5 December 2022).

BS EN 481:1993 Workplace atmospheres. Size fraction definitions for measurement of airborne particles (1993) https://www.en-standard.eu. Available at: https://www.en-standard.eu/bs-en-481-1993-workplace-atmospheres-size-fraction-definitions-for-measurement-of-airborne-particles/ (Accessed: 11 January 2023).

BS EN 12619:2013 Stationary source emissions. Determination of the mass concentration of total gaseous organic carbon. Continuous flame ionisation detector method (2013) https://www.en-standard.eu. Available at: https://www.en-standard.eu/bs-en-12619-2013-stationary-source-emissions-determination-of-the-mass-concentration-of-total-gaseous-organic-carbon-continuous-flame-ionisation-detector-method/ (Accessed: 19 November 2022).

BS EN 13284-1:2017 Stationary source emissions. Determination of low range mass concentration of dust Manual gravimetric method (2017) https://www.en-standard.eu. Available at: https://www.en-standard.eu/bs-en-13284-1-2017-stationary-source-emissions-determination-of-low-range-mass-concentration-of-dust-manual-gravimetric-method/ (Accessed: 19 November 2022).

BS EN 14212:2012 Ambient air. Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence (2012) https://www.en-standard.eu. Available at: https://www.en-standard.eu/bs-en-14212-2012-ambient-air-standard-method-for-the-measurement-of-the-concentration-of-sulphur-dioxide-by-ultraviolet-fluorescence/ (Accessed: 19 November 2022).

BS EN 14791:2017 Stationary source emissions. Determination of mass concentration of sulphur oxides. Standard reference method (2017) https://www.en-standard.eu. Available at: https://www.en-standard.eu/bs-en-14791-2017-stationary-source-emissions-determination-of-mass-concentration-of-sulphur-oxides-standard-reference-method/ (Accessed: 19 November 2022).

BS EN 14792:2017 Stationary source emissions. Determination of mass concentration of nitrogen oxides. Standard reference method. Chemiluminescence (2017) https://www.en-standard.eu. Available at: https://www.en-standard.eu/bs-en-14792-2017-stationary-source-emissions-determination-of-mass-concentration-of-nitrogen-oxides-standard-reference-method-chemiluminescence/ (Accessed: 19 November 2022).

BS EN ISO 20502:2016 Fine ceramics (advanced ceramics, advanced technical ceramics). Determination of adhesion of ceramic coatings by scratch testing (2016) https://www.en-standard.eu. Available at: https://www.en-standard.eu/bs-en-iso-20502-2016-fine-ceramics-advanced-ceramics-advanced-technical-ceramics-determination-of-adhesion-of-ceramic-coatings-by-scratch-testing/ (Accessed: 12 January 2023).

Buffle, J.A.E. (1977) 'Les substances humiques et leurs interactions avec les ions mine´raux.', Tech Sci Munic, (1), pp. 3–10.

Busani, G., Palmonari, C. and Timellini, G. (1995) Ceramic tiles and the Environment: air and water emissions, solid waste and noise. Sassuolo, Italy: EdiCer.

Butera, S., Christensen, T.H. and Astrup, T.F. (2014) 'Composition and leaching of construction and demolition waste: inorganic elements and organic compounds', Journal of Hazardous Materials, 276, pp. 302–311. Available at: https://doi.org/10.1016/j.jhazmat.2014.05.033.

Carbonchi, C. et al. (2013) 'Impiego di fondenti additivati con vetro in un impasto da gres porcellanato', Ceramica Informazione, 426, pp. 580–587.

Carneiro, J. et al. (2018) 'Synthesis of ceramic pigments from industrial wastes: Red mud and electroplating sludge', Waste Management, 80, pp. 371–378. Available at: https://doi.org/10.1016/j.wasman.2018.09.032.

Carty, W. and Pinto, B. (2008) 'Effect of Filler Size on the Strength of Porcelain Bodies', in, pp. 95–105. Available at: https://doi.org/10.1002/9780470294734.ch23.

Carty, W. and Senapati, U. (2005) 'Porcelain—Raw Materials, Processing, Phase Evolution, and Mechanical Behavior', Journal of the American Ceramic Society, 81, pp. 3–20. Available at: https://doi.org/10.1111/j.1151-2916.1998.tb02290.x.

Cavalcante, F. et al. (2007) 'Illite-smectite mixed layers in Sicilide shales and piggy-back deposits of the Gorgoglione Formation (Southern Apennines); geological inferences', Italian Journal of Geosciences, 126(2), pp. 241–254.

Cavalcante, P.M.T. et al. (2009) 'Colour performance of ceramic nano-pigments', Dyes and Pigments, 80(2), pp. 226–232. Available at: https://doi.org/10.1016/j.dyepig.2008.07.004.

Celik, H. (2014) 'The use of tincal calcination plant waste as an additive in ceramic wall tile production', Journal of Ceramic Processing Research, 15(6), pp. 508–513. Available at: https://doi.org/10.36410/jcpr.2014.15.6.508.

Ceramic Manufacturing Industry | Eippcb (2022). Available at: https://eippcb.jrc.ec.europa.eu/reference/ceramic-manufacturing-industry (Accessed: 18 October 2022).

Chen, Y. et al. (2013) 'Preparation and characterization of red porcelain tiles with hematite tailings', Construction and Building Materials, 38, pp. 1083–1088. Available at: https://doi.org/10.1016/j.conbuildmat.2012.06.056.

Chiappone, A. et al. (2004) 'Clay mineral characterization through the methylene blue test: comparison with other experimental techniques and applications of the method', Canadian Geotechnical Journal, 41(6), pp. 1168–1178. Available at: https://doi.org/10.1139/t04-060.

Chowdhury, Md.S. et al. (2020) 'An overview of solar photovoltaic panels' end-of-life material recycling', Energy Strategy Reviews, 27, p. 100431. Available at: https://doi.org/10.1016/j.esr.2019.100431.

Commission Decision (EU) 2021/476 of 16 March 2021 establishing the EU Ecolabel criteria for hard covering products (notified under document C (2021) 1579) (Text with EEA relevance) (2021) OJ L. Available at: http://data.europa.eu/eli/dec/2021/476/oj/eng (Accessed: 21 November 2022).

Corradi, A.B. et al. (1996) 'Quantitative determination of pyrite in, ceramic clay raw materials by DTA', Thermochimica Acta, 287(1), pp. 101–109. Available at: https://doi.org/10.1016/0040-6031(96)02984-X.

Council Directive 91/689/EEC of 12 December 1991 on hazardous waste (1991) OJ L. Available at: http://data.europa.eu/eli/dir/1991/689/oj/eng (Accessed: 17 October 2022).

CSN EN 16165 (2021) https://www.en-standard.eu. Available at: https://www.en-standard.eu/csn-en-16165-determination-of-slip-resistance-of-pedestrian-surfaces-methods-of-evaluation/ (Accessed: 13 January 2023).

Cucchiella, F., D'Adamo, I. and Rosa, P. (2015) 'End-of-Life of used photovoltaic modules: A financial analysis', Renewable & Sustainable Energy Reviews, 47, pp. 552–561. Available at: https://doi.org/10.1016/j.rser.2015.03.076.

Dal Bó, M., Bernardin, A.M. and Hotza, D. (2014) 'Formulation of ceramic engobes with recycled glass using mixture design', Journal of Cleaner Production, 69, pp. 243–249. Available at: https://doi.org/10.1016/j.jclepro.2014.01.088.

Dana, K., Dey, J. and Das, S.K. (2005) 'Synergistic effect of fly ash and blast furnace slag on the mechanical strength of traditional porcelain tiles', Ceramics International, 31(1), pp. 147–152. Available at: https://doi.org/10.1016/j.ceramint.2004.04.008.

Das, S.K. et al. (2013) 'The Effect of Basic Oxygen Furnace Slag and Fly Ash Additions in Triaxial Porcelain Composition: Phase and Micro Structural Evolution', Transactions of the Indian Institute of Metals, 66(3), pp. 213–220. Available at: https://doi.org/10.1007/s12666-013-0245-y.

De Noni, A. et al. (2009) 'Effect of quartz particle size on the mechanical behaviour of porcelain tile subjected to different cooling rates', Journal of the European Ceramic Society, 29(6), pp. 1039–1046. Available at: https://doi.org/10.1016/j.jeurceramsoc.2008.07.052.

Decreto 29 Gennaio 2007 Emanazione di linee guida per l'individuazione e l'utilizzazione delle migliori tecniche disponibili, in materia di fabbricazione di vetro, fritte vetrose e prodotti ceramici, per le attivita' elencate nell'allegato I del decreto legislativo 18 febbraio 2005, n. 59 (2007). Available at:

https://www.ambientediritto.it/Legislazione/INQUINAMENTO/2007/dm_29gen2007_vetro.htm (Accessed: 21 November 2022).

DECRETO LEGISLATIVO 3 aprile 2006, n. 152 - Normattiva (2006). Available at: https://www.normattiva.it/uri-res/N2Ls?urn:nir:stato:decreto.legislativo:2006;152 (Accessed: 18 October 2022).

DECRETO LEGISLATIVO 3 dicembre 2010, n. 205 - Normattiva (2010). Available at: https://www.normattiva.it/uri-res/N2Ls?urn:nir:stato:decreto.legislativo:2010;205 (Accessed: 17 October 2022).

DECRETO LEGISLATIVO 4 marzo 2014, n. 46 - Normattiva (2014). Available at: https://www.normattiva.it/uri-res/N2Ls?urn:nir:stato:decreto-legislativo:2014-03-04;46 (Accessed: 18 October 2022).

Delay, M. et al. (2007) 'Comparison of leaching tests to determine and quantify the release of inorganic contaminants in demolition waste', Waste Management (New York, N.Y.), 27(2), pp. 248–255. Available at: https://doi.org/10.1016/j.wasman.2006.01.013.

Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 establishing a system for greenhouse gas emission allowance trading within the Union and amending Council Directive 96/61/EC (Text with EEA relevance) Text with EEA relevance (2021). Available at: http://data.europa.eu/eli/dir/2003/87/2021-01-01/eng (Accessed: 20 October 2022).

Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control (Codified version) (Text with EEA relevance) (2008) OJ L. Available at: http://data.europa.eu/eli/dir/2008/1/oj/eng (Accessed: 18 October 2022).

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) (2008) OJ L. Available at: http://data.europa.eu/eli/dir/2008/98/oj/eng (Accessed: 26 September 2022).

Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast) (Text with EEA relevance) (2011). Available at: http://data.europa.eu/eli/dir/2010/75/2011-01-06/eng (Accessed: 18 October 2022).

Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE) (recast) (Text with EEA relevance) (2018). Available at: http://data.europa.eu/eli/dir/2012/19/2018-07-04/eng (Accessed: 21 June 2022).

Directive (EU) 2017/2398 of the European Parliament and of the Council of 12 December 2017 amending Directive 2004/37/EC on the protection of workers from the risks related to exposure to carcinogens or mutagens at work (Text with EEA relevance) (2017) OJ L. Available at: http://data.europa.eu/eli/dir/2017/2398/oj/eng (Accessed: 3 October 2022).

Directive (EU) 2018/851 of the European Parliament and of the Council of 30 May 2018 amending Directive 2008/98/EC on waste (Text with EEA relevance) (2018) OJ L. Available at: http://data.europa.eu/eli/dir/2018/851/oj/eng (Accessed: 6 October 2022).

Dondi, M. et al. (1992) 'Carbonatic clays for the production of porous ceramic tiles by fast single firing', Geologica Carpathica - Clays, 2, pp. 91–95.

Dondi, M. et al. (2005) 'The role of surface microstructure on the resistance to stains of porcelain stoneware tiles', Journal of the European Ceramic Society, 25(4), pp. 357–365. Available at: https://doi.org/10.1016/j.jeurceramsoc.2004.01.017.

Dondi, M. (2018) 'Feldspathic fluxes for ceramics: Sources, production trends and technological value', Resources, Conservation and Recycling, 133, pp. 191–205. Available at: https://doi.org/10.1016/j.resconrec.2018.02.027.

Dondi, M. et al. (2019) 'Deposits, composition and technological behavior of fluxes for ceramic tiles', Periodico di Mineralogia, 88(3). Available at: https://doi.org/10.2451/2019PM861.

Dondi, M. et al. (2021) 'Resource efficiency versus market trends in the ceramic tile industry: Effect on the supply chain in Italy and Spain', Resources, Conservation and Recycling, 168, p. 105271. Available at: https://doi.org/10.1016/j.resconrec.2020.105271.

Dondi, M. and Bertolotti, G.P. (2021) 'Basic Guidelines for Prospecting and Technological Assessment of Clays for the Ceramic Industry, Part 1', Interceram - International Ceramic Review, 70(4), pp. 36–46. Available at: https://doi.org/10.1007/s42411-021-0472-x.

Dondi, M., Raimondo, M. and Zanelli, C. (2014) 'Clays and bodies for ceramic tiles: Reappraisal and technological classification', Applied Clay Science, 96, pp. 91–109. Available at: https://doi.org/10.1016/j.clay.2014.01.013.

Ediz, N. and Yurdakul, A. (2009) 'Development of body formulations using colemanite waste in porcelain tile production', Journal of Ceramic Processing Research, 10, pp. 758–769.

Environmental Protection Agency, E.P.A. (2022) EU Emissions Trading System. Available at: https://www.epa.ie/our-services/licensing/climate-change/eu-emissions-trading-system-/ (Accessed: 20 October 2022).

EPA Method TO11A Determination of Formaldehyde in Ambient Air using Adsorbant Cartridge followed by High Performance Liquid Chromatography (HPLC) (1999). Available at: https://www.waters.com/nextgen/us/en/library/application-notes/2008/epa-method-to11-determination-formaldehyde-ambient-air-adsorbant-cartridge-high-performance-liquid-chromatography-hplc.html (Accessed: 19 November 2022).

EPD Italy (no date). Available at: https://www.epditaly.it/ricerca-epd/ (Accessed: 25 November 2022).

EPD the environmental product declaration for Italian ceramic tiles - Confindustria Ceramica (2023). Available at: http://www.confindustriaceramica.it/site/en/home/news/articolo8548.html (Accessed: 11 January 2023).

European Industrial Emissions Portal (2022). Available at: https://industry.eea.europa.eu (Accessed: 28 January 2023).

Feola, G. (2020) 'Capitalism in sustainability transitions research: Time for a critical turn?', Environmental Innovation and Societal Transitions, 35, pp. 241–250. Available at: https://doi.org/10.1016/j.eist.2019.02.005.

Ferrari, S. and Gualtieri, A.F. (2006) 'The use of illitic clays in the production of stoneware tile ceramics', Applied Clay Science, 32(1), pp. 73–81. Available at: https://doi.org/10.1016/j.clay.2005.10.001.

Fischer, U. et al. (2015) 'Investigation of Glaze Layer Formation on Green Ceramic Bodies', International Journal of Applied Ceramic Technology, 12(1), pp. 81–94. Available at: https://doi.org/10.1111/ijac.12122.

Fiume, M.M. et al. (2015) 'Safety Assessment of Talc as Used in Cosmetics', International Journal of Toxicology, 34(1 Suppl), pp. 66S-129S. Available at: https://doi.org/10.1177/1091581815586797.

'Fly Ash | Buildex' (2022). Available at: https://buildexgroup.net/fly-ash/ (Accessed: 8 October 2022).

Fontes, W.C. et al. (2019) 'Assessment of the use potential of iron ore tailings in the manufacture of ceramic tiles: From tailings-dams to "brown porcelain"', Construction and Building Materials, 206, pp. 111–121. Available at: https://doi.org/10.1016/j.conbuildmat.2019.02.052.

Front page | Eippcb (2022). Available at: https://eippcb.jrc.ec.europa.eu/ (Accessed: 18 October 2022).

Galos, K. (2011) 'Influence of mineralogical composition of applied ball clays on properties of porcelain tiles', Ceramics International, 37(3), pp. 851–861. Available at: https://doi.org/10.1016/j.ceramint.2010.10.014.

Gardini, D. et al. (2008) 'Nano-sized ceramic inks for drop-on-demand ink-jet printing in quadrichromy', Journal of Nanoscience and Nanotechnology, 8(4), pp. 1979–1988. Available at: https://doi.org/10.1166/jnn.2008.048.

Gardini, D. et al. (2015) 'Ceramic Ink-Jet Printing for Digital Decoration: Physical Constraints for Ink Design', Journal of Nanoscience and Nanotechnology, 15(5), pp. 3552–3561. Available at: https://doi.org/10.1166/jnn.2015.9857.

Gazzetta Ufficiale (no date). Available at: https://www.gazzettaufficiale.it/dettaglio/codici/materiaAmbientale (Accessed: 6 October 2022).

Geos 306, Fall 2004, Lecture 13, The Crust (2022). Available at: https://www.geo.arizona.edu/xtal/geos306/fall04-13.htm (Accessed: 4 October 2022).

Gilbertson, T. (2009) 'How sustainable are small-scale biomass factories? A case study from Thailand. In S. Böhm and S. Dabhi (Eds.)', in Upsetting the offset: the political economy of carbon markets. London: Mayfly, pp. 57–71. Available at: http://mayflybooks.org/?page_id=21.

Guzmán A, Á. et al. (2015) 'Valorization of rice straw waste: production of porcelain tiles', Cerâmica, 61, pp. 442–449. Available at: https://doi.org/10.1590/0366-69132015613601939.

Hajjaji, W. et al. (2012) 'An overview of using solid wastes for pigment industry', Journal of the European Ceramic Society, 32(4), pp. 753–764. Available at: https://doi.org/10.1016/j.jeurceramsoc.2011.10.018.

Haldar, S.K.K. (2020) Introduction to Mineralogy and Petrology. Elsevier.

Harlow, B.L. and Hartge, P.A. (1995) 'A Review of Perineal Talc Exposure and Risk of Ovarian Cancer'. Available at: https://doi.org/10.1006/rtph.1995.1039.

Henderson, W.J. et al. (1971) 'Talc and Carcinoma of the Ovary and Cervix', BJOG: An International Journal of Obstetrics & Gynaecology, 78(3), pp. 266–272. Available at: https://doi.org/10.1111/j.1471-0528.1971.tb00267.x.

Higgins, L.M., Bauer, W.H. and Carr, D.S. (1979) 'Utilization of lead and zinc slags in ceramic construction products', Conservation & Recycling, 3(3), pp. 375–382. Available at: https://doi.org/10.1016/0361-3658(79)90036-5.

Home | Sustainable Development (2022). Available at: https://sdgs.un.org/ (Accessed: 11 October 2022).

Home - Confindustria Ceramica (2022). Available at: http://www.confindustriaceramica.it/site/home.html (Accessed: 24 October 2022).

Homepage - Autorizzazione Integrata Ambientale - Regione Emilia Romagna (2022). Available at: http://ippc-aia.arpa.emr.it/ippc-aia/Intro.aspx (Accessed: 18 October 2022).

Incinerator Bottom Ash – Preparation, Testing and Monitoring (2022) SOCOTEC UK. Available at: https://www.socotec.co.uk/our-services/energy-supply-generation-and-regulation/incinerator-bottom-ash-preparation-testing-and-monitoring (Accessed: 8 October 2022).

Indagine statistica sull’industria italiana - piastrelle di ceramica - Confindustria Ceramica (2019). Available at: http://www.confindustriaceramica.it/site/home/bookstore/studi-di-settore/indagine-statistica-sullindustria-italiana----piastrelle-di-ceramica.html (Accessed: 27 January 2023).

ISO (1994a) ISO 10545-8:1994, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/00/18/1813.html (Accessed: 26 October 2022).

ISO (1994b) ISO 10545-11:1994, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/01/86/18624.html (Accessed: 26 October 2022).

ISO (1995a) ISO 10545-2:1995, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/01/86/18616.html (Accessed: 26 October 2022).

ISO (1995b) ISO 10545-12:1995, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/01/86/18625.html (Accessed: 26 October 2022).

ISO (1996a) ISO 10545-5:1996, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/01/86/18619.html (Accessed: 26 October 2022).

ISO (1996b) ISO 10545-7:1996, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/01/86/18621.html (Accessed: 26 October 2022).

ISO (2000) ISO 14020:2000, ISO. Available at: https://www.iso.org/standard/34425.html (Accessed: 25 November 2022).

ISO (2006) ISO 14025:2006, ISO. Available at: https://www.iso.org/standard/38131.html (Accessed: 5 December 2022).

ISO (2010a) ISO 7619-1:2010, ISO. Available at: https://www.iso.org/standard/50756.html (Accessed: 12 January 2023).

ISO (2010b) ISO 10545-6:2010, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/05/10/51089.html (Accessed: 26 October 2022).

ISO (2010c) ISO 10545-16:2010, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/05/10/51090.html (Accessed: 26 October 2022).

ISO (2013) ISO 10545-9:2013, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/05/72/57241.html (Accessed: 26 October 2022).

ISO (2014a) ISO 6506-1:2014, ISO. Available at: https://www.iso.org/standard/59671.html (Accessed: 12 January 2023).

ISO (2014b) ISO 10545-1:2014, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/06/09/60974.html (Accessed: 26 October 2022).

ISO (2015a) ISO 6508-1:2015, ISO. Available at: https://www.iso.org/standard/59686.html (Accessed: 12 January 2023).

ISO (2015b) ISO 10545-14:2015, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/06/09/60972.html (Accessed: 26 October 2022).

ISO (2016a) ISO 10545-13:2016, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/06/09/60975.html (Accessed: 26 October 2022).

ISO (2016b) ISO 14021:2016, ISO. Available at: https://www.iso.org/standard/66652.html (Accessed: 5 December 2022).

ISO (2017) ISO 4545-1:2017, ISO. Available at: https://www.iso.org/standard/63982.html (Accessed: 12 January 2023).

ISO (2018a) ISO 6507-1:2018, ISO. Available at: https://www.iso.org/standard/64065.html (Accessed: 12 January 2023).

ISO (2018b) ISO 10545-3:2018, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/06/80/68006.html (Accessed: 26 October 2022).

ISO (2018c) ISO 14024:2018, ISO. Available at: https://www.iso.org/standard/72458.html (Accessed: 5 December 2022).

ISO (2019) ISO 10545-4:2019, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/06/96/69619.html (Accessed: 26 October 2022).

ISO (2021a) ISO 10545-10:2021, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/07/22/72272.html (Accessed: 26 October 2022).

ISO (2021b) ISO 10545-15:2021, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/07/22/72271.html (Accessed: 26 October 2022).

ISO (2021c) ISO 17889-1:2021, ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/07/43/74306.html (Accessed: 14 November 2022).

ISO (2022a) ISO 10545-18:2022, ISO. Available at: https://www.iso.org/standard/76633.html (Accessed: 12 January 2023).

ISO (2022b) ISO 10545-20:2022, ISO. Available at: https://www.iso.org/standard/76634.html (Accessed: 12 January 2023).

ISO 13006:2018 (2018) ISO. Available at: https://www.iso.org/cms/render/live/en/sites/isoorg/contents/data/standard/06/34/63406.html (Accessed: 21 October 2022).

ISTISAN 88/19 Campionamento e dosaggio di microinquinanti in flussi gassosi convogliati (1988) ISS. Available at: https://iss.it/rapporti-istisan (Accessed: 19 November 2022).

ISTISAN 98/2 (DM 25/08/00 Allegato 1) (1998) ISS. Available at: https://iss.it/rapporti-istisan/-/asset_publisher/Ga8fOpve0fNN/content/98-2-gruppo-di-lavoro-istituto-superiore-di-sanit%C3%A0-%3Cquote%3Emetodiche-per-il-rilevamento-delle-emissioni-in-atmosfera-da-impianti-industriali%3C-quote%3E-rilevamento-delle-emissioni-in-flussi-gassosi-convogliati.-a-ossidi-di-zolfo-e-ossidi-di-azoto (Accessed: 19 November 2022).

ISTISAN 98/2 (DM 25/08/00 Allegato 2) (no date) ISS. Available at: https://iss.it/rapporti-istisan/-/asset_publisher/Ga8fOpve0fNN/content/98-2-gruppo-di-lavoro-istituto-superiore-di-sanit%C3%A0-%3Cquote%3Emetodiche-per-il-rilevamento-delle-emissioni-in-atmosfera-da-impianti-industriali%3C-quote%3E-rilevamento-delle-emissioni-in-flussi-gassosi-convogliati.-a-ossidi-di-zolfo-e-ossidi-di-azoto (Accessed: 19 November 2022).

Kallay, N. (2000) Interfacial Dynamics. CRC Press.

Karadagli, E. and Cicek, B. (2020) 'Boron mining and enrichment waste: A promising raw material for porcelain tile production', International Journal of Applied Ceramic Technology, 17(2), pp. 563–572. Available at: https://doi.org/10.1111/ijac.13438.

Kats, M.É. and Kvyatkovskaya, K.K. (1972) 'Low temperature flux compositions for the production of cast ceramic tile', Glass and Ceramics, 29(2), pp. 101–103. Available at: https://doi.org/10.1007/BF00677500.

Kavanova, M. (2017) 'Characterization of the interaction between glazes and ceramic bodies', Ceramics - Silikaty, 61, pp. 1–10. Available at: https://doi.org/10.13168/cs.2017.0025.

Kaza, S. et al. (2018) What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050. Washington, DC: World Bank. Available at: https://doi.org/10.1596/978-1-4648-1329-0.

Kim, B. and Prezzi, M. (2008) 'Evaluation of the mechanical properties of class-F fly ash', Waste Management, 28(3), pp. 649–659. Available at: https://doi.org/10.1016/j.wasman.2007.04.006.

Kim, Kidong, Kim, Kicheol and Hwang, J. (2016) 'Characterization of ceramic tiles containing LCD waste glass', Ceramics International, 42(6), pp. 7626–7631. Available at: https://doi.org/10.1016/j.ceramint.2016.01.172.

Korç, G.Ç. et al. (2018) 'Development of low temperature porcelain tile bodies with low-grade boron bearing minerals by dry route', p. 10.

Lagaly, G. (1989) 'Principles of flow of kaolin and bentonite dispersions', Applied Clay Science, 4(2), pp. 105–123. Available at: https://doi.org/10.1016/0169-1317(89)90003-3.

Lazaro, C. et al. (2012) 'Development of New Ecological Ceramic Tiles by Recycling of Waste Glass and Ceramic Materials', Boletin De La Sociedad Espanola De Ceramica Y Vidrio, 51(2), pp. 139–144. Available at: https://doi.org/10.3989/cyv.202012.

Lee, S., Kim, Y.J. and Moon, H.-S. (1999) 'Phase Transformation Sequence from Kaolinite to Mullite Investigated by an Energy-Filtering Transmission Electron Microscope', Journal of the American Ceramic Society, 82(10), pp. 2841–2848. Available at: https://doi.org/10.1111/j.1151-2916.1999.tb02165.x.

Leonelli, C. et al. (2001) 'Enhancing the mechanical properties of porcelain stoneware tiles: a microstructural approach', Journal of the European Ceramic Society, 21(6), pp. 785–793. Available at: https://doi.org/10.1016/S0955-2219(00)00266-1.

Leung, C.C., Yu, I.T.S. and Chen, W. (2012) 'Silicosis', The Lancet, 379(9830), pp. 2008–2018. Available at: https://doi.org/10.1016/S0140-6736(12)60235-9.

Ligabue, M.L. et al. (2020) 'Recycling of thermally treated cement-asbestos for the production of porcelain stoneware slabs', Journal of Cleaner Production, 247, p. 119084. Available at: https://doi.org/10.1016/j.jclepro.2019.119084.

List of Classifications – IARC Monographs on the Identification of Carcinogenic Hazards to Humans (2022). Available at: https://monographs.iarc.who.int/list-of-classifications (Accessed: 4 October 2022).

Magagnin, D. et al. (2014) 'Effect of kaolinite, illite and talc on the processing properties and mullite content of porcelain stoneware tiles', Materials Science and Engineering: A, 618, pp. 533–539. Available at: https://doi.org/10.1016/j.msea.2014.09.049.

Mancy (2020) 'Ceramic Ball Mill for Sale | Buy Ceramic Ball Mill Machine with Good Performance', AGICO Mining and Cement Milling Equipment | Ball Mill for Sale, 2 July. Available at: https://ballmillssupplier.com/product-center/ceramic-ball-mill/ (Accessed: 5 October 2022).

Manfredini, T. et al. (1991) 'The recycling of ceramic sludges in the production process: An option for ceramic tile factories to reach zero pollution', Environmental Technology, 12(10), pp. 927–934. Available at: https://doi.org/10.1080/09593339109385088.

Martín-Márquez, J. et al. (2009) 'Evolution with Temperature of Crystalline and Amorphous Phases in Porcelain Stoneware', Journal of the American Ceramic Society, 92(1), pp. 229–234. Available at: https://doi.org/10.1111/j.1551-2916.2008.02862.x.

Massari, S. and Ruberti, M. (2013) 'Rare earth elements as critical raw materials: Focus on international markets and future strategies', Resources Policy, 38(1), pp. 36–43. Available at: https://doi.org/10.1016/j.resourpol.2012.07.001.

Matteucci, F., Dondi, M. and Guarini, G. (2002) 'Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles', Ceramics International, 28(8), pp. 873–880. Available at: https://doi.org/10.1016/S0272-8842(02)00067-6.

Medina, C., Sánchez de Rojas, M.I. and Frías, M. (2013) 'Freeze-thaw durability of recycled concrete containing ceramic aggregate', Journal of Cleaner Production, 40, pp. 151–160. Available at: https://doi.org/10.1016/j.jclepro.2012.08.042.

Mehta, A. and Siddique, R. (2016) 'An overview of geopolymers derived from industrial by-products', Construction and Building Materials, 127, pp. 183–198. Available at: https://doi.org/10.1016/j.conbuildmat.2016.09.136.

Mindat.org (2022). Available at: https://www.mindat.org/ (Accessed: 4 October 2022).

Mineral Resources Program | U.S. Geological Survey (2022). Available at: https://www.usgs.gov/programs/mineral-resources-program (Accessed: 4 October 2022).

Minguillón, M.C. et al. (2007) 'PM10 speciation and determination of air quality target levels. A case study in a highly industrialized area of Spain', Science of The Total Environment, 372(2), pp. 382–396. Available at: https://doi.org/10.1016/j.scitotenv.2006.10.023.

Minguillón, M.C. et al. (2009) 'Effect of ceramic industrial particulate emission control on key components of ambient PM10', Journal of Environmental Management, 90(8), pp. 2558–2567. Available at: https://doi.org/10.1016/j.jenvman.2009.01.016.

Minguillón, M.C. et al. (2013) 'Air quality comparison between two European ceramic tile clusters', Atmospheric Environment, 74, pp. 311–319. Available at: https://doi.org/10.1016/j.atmosenv.2013.04.010.

Mohs Hardness Scale: Testing the Resistance to Being Scratched (2022). Available at: https://geology.com/minerals/mohs-hardness-scale.shtml (Accessed: 12 January 2023).

Mokrzycki, W. and Tatol, M. (2011) 'Color difference Delta E - A survey', Machine Graphics and Vision, 20, pp. 383–411.

Monfort, E. et al. (2008) 'Evolution of fluorine emissions during the fast firing of ceramic tile', Applied Clay Science, 38(3), pp. 250–258. Available at: https://doi.org/10.1016/j.clay.2007.03.001.

Moshnyakov, M.G. and Abdrakhimov, V.Z. (2019) 'Investigations of the Black Core and Swelling in Firing Porcelain Stoneware', Glass and Ceramics, 76(7), pp. 270–273. Available at: https://doi.org/10.1007/s10717-019-00181-8.

Naga, S.M. et al. (2014) 'Recycling of Fish Bone Ash in the Preparation of Stoneware Tiles', Interceram - International Ceramic Review, 63(1), pp. 15–18. Available at: https://doi.org/10.1007/BF03401028.

Nandi, V.S. et al. (2015) 'The use of ceramic sludge and recycled glass to obtain engobes for manufacturing ceramic tiles', Journal of Cleaner Production, 86, pp. 461–470. Available at: https://doi.org/10.1016/j.jclepro.2014.08.091.

Navarro, J.M.F. (2003) El vidrio. Editorial CSIC - CSIC Press.

NIOSH 2539, Issue 2 (1994). Available at: https://commons.wikimedia.org/wiki/File:NIOSH_Manual_of_Analytical_Methods_-_2539.pdf (Accessed: 19 November 2022).

NIOSH 2541, Issue 2 (1994). Available at: https://commons.wikimedia.org/wiki/File:NIOSH_Manual_of_Analytical_Methods_-_2541.pdf (Accessed: 19 November 2022).

O'Brien, P.J., Siraki, A.G. and Shangari, N. (2005) 'Aldehyde sources, metabolism, molecular toxicity mechanisms, and possible effects on human health', Critical Reviews in Toxicology, 35(7), pp. 609–662. Available at: https://doi.org/10.1080/10408440591002183.

OPEN DATA INAIL - Quali dati (2023). Available at: https://dati.inail.it/opendata/default/Qualidati/index.html (Accessed: 6 January 2023).

Pal, M. et al. (2016) 'Thermal analysis and vitrification behavior of slag containing porcelain stoneware body', Journal of Thermal Analysis and Calorimetry, 124(3), pp. 1169–1177. Available at: https://doi.org/10.1007/s10973-015-5179-7.

Palmonari, C. (1979) Inquinamento atmosferico da Industrie Ceramiche: Studio di un Comprensorio: Sassuolo. Bologna, Italy: Centro Ceramico.

Palmonari, C. and Timellini, G. (2000) 'The environmental impact of the ceramic tile industry. New Approaches to the management in Europe.', Journal of the Australasian Ceramic Society, 36(2), pp. 23–33.

Panya, P. et al. (2005) 'The Effect of Ionic Surfactant Adsorption on the Rheology of Ceramic Glaze Suspensions', Journal of the American Ceramic Society, 88(3), pp. 540–546. Available at: https://doi.org/10.1111/j.1551-2916.2005.00121.x.

Parisotto, A. et al. (2021) ‘Colorimetric evaluation of the presence of efflorescence in red clay ceramics with calcium and sulfate ions’, Ceramics International, 47(11), pp. 16186–16191. Available at: https://doi.org/10.1016/j.ceramint.2021.02.196.

Peterson, M. et al. (2007) ‘Evaluation of the steger method in the determination of ceramic-glaze joining’, Materials Science and Engineering: A, 466(1), pp. 183–186. Available at: https://doi.org/10.1016/j.msea.2007.02.046.

Piastrelle di Ceramica e Refrattari - Rapporto Integrato 1998 - Ambiente, Energia, Sicurezza-Salute, Qualità (1998). Sassuolo, Italy: Assopiastrelle-Snam.

Plant, J.A., Voulvoulis, N. and Ragnarsdottir, K.V. (2012) Pollutants, Human Health and the Environment: A Risk Based Approach. John Wiley & Sons.

Ponsot, I., Falcone, R. and Bernardo, E. (2013) ‘Stabilization of fluorine-containing industrial waste by production of sintered glass-ceramics’, Ceramics International, 39(6), pp. 6907–6915. Available at: https://doi.org/10.1016/j.ceramint.2013.02.025.

Pontikes, Y. et al. (2005) ‘Use of scrap soda–lime–silica glass in traditional ceramics’, Glass Technology - European Journal of Glass Science and Technology Part A, 46, pp. 200–206.

Porter, M.E. and van der Linde, C. (1995) ‘Toward a New Conception of the Environment-Competitiveness Relationship’, The Journal of Economic Perspectives, 9(4), pp. 97–118.

Pradell, T. and Molera, J. (2020) ‘Ceramic technology. How to characterise ceramic glazes’, Archaeological and Anthropological Sciences, 12(8), p. 189. Available at: https://doi.org/10.1007/s12520-020-01136-9.

Prasartseree, T. et al. (2018) ‘Influence of Lignite Bottom Ash on Pyroplastic Deformation of Stoneware Ceramic Tiles’, Key Engineering Materials, 766, pp. 264–269. Available at: https://doi.org/10.4028/www.scientific.net/KEM.766.264.

PubChem (2022) PubChem. Available at: https://pubchem.ncbi.nlm.nih.gov/ (Accessed: 30 September 2022).

Raimondo, M. et al. (2007) ‘Effect of waste glass (TV/PC cathodic tube and screen) on technological properties and sintering behaviour of porcelain stoneware tiles’, Ceramics International, 33(4), pp. 615–623. Available at: https://doi.org/10.1016/j.ceramint.2005.11.012.

Rambaldi, E. et al. (2010) ‘The recycling of MSWI bottom ash in silicate based ceramic’, Ceramics International, 36(8), pp. 2469–2476. Available at: https://doi.org/10.1016/j.ceramint.2010.08.005.

Rambaldi, E et al. (2018) ‘High-recycling content porcelain stoneware tiles: from industrial production to product certificaition’. Proceeding of the Qualicer 2018 Congress, Castellòn (Spain). Available at: http://www.wincer-project.eu/wp-content/uploads/2018/02/PAPER-Qualicer-2018_65_PON_ING.pdf.

Rambaldi, E. et al. (2018) ‘Highrecycling content porcelain stoneware tiles: from industrial production to product certification’. Proceedings of the Qualicer 2018 Congress, Castellòn (Spain).

Ray, S. et al. (2021) ‘Use of ceramic wastes as aggregates in concrete production: A review’, Journal of Building Engineering, 43, p. 102567. Available at: https://doi.org/10.1016/j.jobe.2021.102567.

Resca, R. et al. (2021) Industrie produttrici di piastrelle di ceramica: fattori di impatto e prestazioni ambientali, 2010-2019. Confindustria Ceramica and Centro Ceramico.

Rey-Raap, N. and Gallardo, A. (2012) 'Determination of mercury distribution inside spent compact fluorescent lamps by atomic absorption spectrometry', Waste Management, 32(5), pp. 944–948. Available at: https://doi.org/10.1016/j.wasman.2011.12.001.

Rieder, M. et al. (1998) 'Nomenclature of the Micas', Clays and Clay Minerals, 46(5), pp. 586–595. Available at: https://doi.org/10.1346/CCMN.1998.0460513.

Rodrigues, F. et al. (2013) 'Physical–chemical and mineralogical characterization of fine aggregates from construction and demolition waste recycling plants', Journal of cleaner production, 52, pp. 438–445. Available at: https://doi.org/10.1016/j.jclepro.2013.02.023.

Ros-Dosdá, T. et al. (2018) 'Environmental profile of Spanish porcelain stoneware tiles', The International Journal of Life Cycle Assessment, 23(8), pp. 1562–1580. Available at: https://doi.org/10.1007/s11367-017-1377-9.

Ros-Dosdá, T. et al. (2019) 'Environmental comparison of indoor floor coverings', Science of The Total Environment, 693, p. 133519. Available at: https://doi.org/10.1016/j.scitotenv.2019.07.325.

SACMI (2001) Applied ceramic technology. Imola (BO): La Mandragora s.r.l.

Sanchez, E. et al. (1998) 'Effect of the kaolin proportion contained in the glaze layer on glaze behaviour in firing', in. QUALIcer 98, Castellòn (Spain).

Sánchez, E. et al. (2010) 'Porcelain tile: Almost 30 years of steady scientific-technological evolution', Ceramics International, 36(3), pp. 831–845. Available at: https://doi.org/10.1016/j.ceramint.2009.11.016.

Sander, K. (2007) 'Study on the development of a take back and recovery system for photovoltaic products'. Ökopol GmbH, Hamburg.

Savvilotidou, V., Hahladakis, J.N. and Gidarakos, E. (2014) 'Determination of toxic metals in discarded Liquid Crystal Displays (LCDs)', Resources, Conservation and Recycling, 92, pp. 108–115. Available at: https://doi.org/10.1016/j.resconrec.2014.09.002.

Schettino, M. and Holanda, J. (2015) 'Processing of porcelain stoneware tile using sugarcane bagasse ash waste', Processing and Application of Ceramics, 9(1), pp. 17–22. Available at: https://doi.org/10.2298/PAC1501017S.

Schmitz, R.M., Schroeder, C. and Charlier, R. (2004) 'Chemo–mechanical interactions in clay: a correlation between clay mineralogy and Atterberg limits', Applied Clay Science, 26(1), pp. 351–358. Available at: https://doi.org/10.1016/j.clay.2003.12.015.

Seinfeld, J.H. (2015) 'Atmospheric Chemistry', in Reference Module in Chemistry, Molecular Sciences and Chemical Engineering. Elsevier. Available at: https://doi.org/10.1016/B978-0-12-409547-2.11626-9.

Siddiqui, A.R. et al. (2014) 'Iron and steel slag: an alternative source of raw materials for porcelain ceramics', Global Nest Journal, 16(4), pp. 587–596.

Silva, R.V. et al. (2017) 'The role of glass waste in the production of ceramic-based products and other applications: A review', Journal of Cleaner Production, 167, pp. 346–364. Available at: https://doi.org/10.1016/j.jclepro.2017.08.185.

Singh, M. and Siddique, R. (2013) 'Effect of coal bottom ash as partial replacement of sand on properties of concrete', Resources, Conservation and Recycling, 72, pp. 20–32. Available at: https://doi.org/10.1016/j.resconrec.2012.12.006.

Skerratt, G. (2001) ‘The commercial manufacture of a tile containing 95% recycled glass cullet’, in Recycling and Reuse of Glass Cullet. Thomas Telford Publishing, pp. 103–108. Available at: https://doi.org/10.1680/rarogc.29941.0011.

Snapshot of Global PV Markets 2022 (no date) IEA-PVPS. Available at: https://iea-pvps.org/snapshot-reports/snapshot-2022/ (Accessed: 17 June 2022).

Società Ceramica Italiana (1984) Reologia ceramica applicata. Faenza: Faenza Ed.

Song, Q., Li, J. and Zeng, X. (2015) ‘Minimizing the increasing solid waste through zero waste strategy’, Journal of Cleaner Production, 104, pp. 199–210. Available at: https://doi.org/10.1016/j.jclepro.2014.08.027.

‘Spray driers’ (2002) ICF & Welko. Available at: https://www.icf-welko.it/en/ceramic/products/grinding-and-spray-drying/spray-driers/ (Accessed: 5 October 2022).

Stevenson, F.J. (1982) Humus chemistry: genesis, composition, reactions. New York: Wiley. Available at: http://catdir.loc.gov/catdir/enhancements/fy0607/81012933-t.html (Accessed: 30 September 2022).

Tarhan, M. and Tarhan, B. (2020) ‘Development of waterproof engobe layer for ceramic wall tiles’, Journal of Thermal Analysis and Calorimetry, 140(2), pp. 555–565. Available at: https://doi.org/10.1007/s10973-019-08893-3.

Taylor, J.R. and Bull, A.C. (1986) Ceramics Glaze Technology. Institute of Ceramics by Pergamon Press.

Timellini, G. et al. (2008) 2° Rapporto Integrato per il Settore delle Piastrelle di Ceramica: Ambiente, Energia, Sicurezza-Salute, Qualità,Responsabilità Sociale d’Impresa. Sassuolo, Italy: Confindustria Ceramica and Centro Ceramico.

Timellini, G., Resca, R. and Bignozzi, M.C. (2016) ‘Chapter 26 - Ceramic Industry Air Quality. Emissions Into the Atmosphere From Ceramic Tile Processes’, in M. de la Guardia and S. Armenta (eds) Comprehensive Analytical Chemistry. Elsevier (The Quality of Air), pp. 707–729. Available at: https://doi.org/10.1016/bs.coac.2016.04.005.

Tucci, A. et al. (2004) ‘Use of soda-lime scrap-glass as a fluxing agent in a porcelain stoneware tile mix’, Journal of the European Ceramic Society, 24(1), pp. 83–92. Available at: https://doi.org/10.1016/S0955-2219(03)00121-3.

Tucci, A., Rambaldi, E. and Esposito, L. (2006) ‘Use of scrap glass as raw material for porcelain stoneware tiles’, Advances in Applied Ceramics, 105(1), pp. 40–45. Available at: https://doi.org/10.1179/174367606X81713.

UNFCCC (2022). Available at: https://unfccc.int/ (Accessed: 11 October 2022).

UNI 10169:2001 - UNI Ente Italiano di Normazione (2001). Available at: https://store.uni.com/uni-10169-2001 (Accessed: 16 January 2023).

UNI 10246-1 : 1993 Emission control - Determination of sulphur oxides (1993). Available at: https://infostore.saiglobal.com/en-us/Standards/UNI-10246-1-1993-1086897_SAIG_UNI_UNI_2530733/ (Accessed: 19 November 2022).

UNI 10568:1997 - UNI Ente Italiano di Normazione (1997). Available at: https://store.uni.com/en/uni-10568-1997-74899.html (Accessed: 19 January 2023).

UNI 10787:1999 - UNI Ente Italiano di Normazione (no date). Available at: https://store.uni.com/uni-10787-1999 (Accessed: 19 November 2022).

UNI 10878 : 2000 Emission measurement - Determination of nitric oxide (NO and NO2) in conveyed gass flows (2000). Available at: https://infostore.saiglobal.com/en-gb/standards/uni-10878-2000-1091945_saig_uni_uni_2541660/ (Accessed: 19 November 2022).

UNI EN 13284-1:2003 - UNI Ente Italiano di Normazione (2003). Available at: https://store.uni.com/uni-en-13284-1-2003 (Accessed: 19 November 2022).

UNI EN 13284-1:2017 - UNI Ente Italiano di Normazione (2017). Available at: https://store.uni.com/uni-en-13284-1-2017 (Accessed: 16 January 2023).

UNI EN 13526:2002 - UNI Ente Italiano di Normazione (2002). Available at: https://store.uni.com/uni-en-13526-2002 (Accessed: 19 November 2022).

UNI EN 13649:2002 - UNI Ente Italiano di Normazione (2002). Available at: https://store.uni.com/uni-en-13649-2002 (Accessed: 19 November 2022).

UNI EN 14385:2004 - UNI Ente Italiano di Normazione (2004). Available at: https://store.uni.com/uni-en-14385-2004 (Accessed: 16 January 2023).

UNICHIM 723/1986 (1986). Available at: https://arpalazio.infoteca.it/ricerca/dettaglio/misure-alle-emissioni/1672 (Accessed: 19 November 2022).

United Nations Treaty Collection (2022). Available at: https://treaties.un.org/pages/ViewDetails.aspx?src=TREATY&mtdsg_no=XXVII-7-d&chapter=27&clang=_en (Accessed: 6 October 2022).

US EPA, O. (2014) Coal Ash Basics. Available at: https://www.epa.gov/coalash/coal-ash-basics (Accessed: 8 October 2022).

USGBC | U.S. Green Building Council (no date). Available at: https://www.usgbc.org/ (Accessed: 5 December 2022).

Vergilio, C. dos S. et al. (2020) 'Metal concentrations and biological effects from one of the largest mining disasters in the world (Brumadinho, Minas Gerais, Brazil)', Scientific Reports, 10, p. 5936. Available at: https://doi.org/10.1038/s41598-020-62700-w.

Vilarinho, I.S. et al. (2021) 'A New Added-Value Application for Steel Wire Drawing Mill Scale Waste in Stoneware Ceramic Products', Metals, 11(4), p. 661. Available at: https://doi.org/10.3390/met11040661.

Vogel, W. (1994) Glass Chemistry. 2nd revised edition. Springer-Verlag Berlin and Heidelberg GmbH & Co. K.

Wilson, I.R. (1998) 'The constitution, evaluation and ceramic properties of ball clays', Cerâmica [Preprint]. Available at: https://doi.org/10.1590/S0366-69131998000400002.

World Commission on Environment and Development (1987) Our common future. Oxford ; New York : Oxford University Press. Available at: http://archive.org/details/ourcommonfuture00worl (Accessed: 11 October 2022).

Zacco, A. et al. (2014) 'Review of fly ash inertisation treatments and recycling', Environmental Chemistry Letters, 12(1), pp. 153–175. Available at: https://doi.org/10.1007/s10311-014-0454-6.

Zanelli, C. et al. (2011) 'The vitreous phase of porcelain stoneware: Composition, evolution during sintering and physical properties', Journal of Non-Crystalline Solids, 357(16), pp. 3251–3260. Available at: https://doi.org/10.1016/j.jnoncrysol.2011.05.020.

Zanelli, C. et al. (2019) 'Recycling of residual boron muds into ceramic tiles', Boletín de la Sociedad Española de Cerámica y Vidrio, 58(5), pp. 199–210.

Zanelli, C. et al. (2021) 'Waste recycling in ceramic tiles: a technological outlook', Resources, Conservation and Recycling, 168, p. 105289. Available at: https://doi.org/10.1016/j.resconrec.2020.105289.

Zhao, L. et al. (2015) 'Synthesis of steel slag ceramics: chemical composition and crystalline phases of raw materials', International Journal of Minerals, Metallurgy, and Materials, 22(3), pp. 325–333. Available at: https://doi.org/10.1007/s12613-015-1077-z.

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