Research paper

Clays and bodies for ceramic tiles: Reappraisal and technological classification

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A B S T R A C T

The ceramic tile industry is a dynamic sector whose technological innovation and market trends have drawn a complex picture of products and processes. Raw materials have been deeply involved in such an evolution: the flexibility of current manufacturing cycles enables the use of a very wide range of clays, whose chemical and mineralogical composition, particle size distribution and ceramic properties were reappraised. The classical reference schemes are no longer able to properly describe and predict the role of clays in tilemaking. In order to fill this gap, an industry-oriented, technological classification of clay raw materials is proposed on the basis of chemical (Fe₂O₃ content) and mineralogical parameters (amount of phyllosilicates and carbonates) together with particle size (fractions <2 μm and >63 μm) and plasticity (methylen blue index and Atterberg plastic index). It firstly discriminates light-firing and dark-firing clays according to an iron oxide threshold of 3%. Light-firing clays are distinguished by the amount of kaolinite group minerals and plasticity in “kaolins” (high-grade, low-grade, and raw kaolins, kaolinitic loams) and “plastic clays” (ball clays, pyrophyllitic clays, white bentonites); the distinction of three classes of ball clays with increasing plasticity is envisaged. Dark-firing clays are classified according to coarse-grained fraction and amount of carbonates in carbonate-rich types (marly and carbonate clays), red loams and red clays; these latter are furtherly differentiated by the relative abundance of clay minerals. Such a classification is essential to draw the guidelines for body formulation and to explain the criteria followed in the industrial practice for each category of ceramic tiles. Key properties are discussed to design batches for porous tiles, vitrified and semi-vitrified red stoneware, and vitrified light-firing bodies. Both the clay classification and the guidelines to body formulation are intended to provide up-to-date tools to assess the ceramic potential and correct use in tilemaking of clay materials, but they cannot substitute a thorough understanding of manufacturing and products already produced with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking (Diaz Rodríguez and Torrecillas, 2002; Harvey and Murray, 1997; McCuistion and Wilson, 2006; Mitchell and Vincent, 1997; Worrall, 1975) or to address the correct design criteria for batch formulation (Fabbri and Fiori, 1985; Fiori et al., 1988; Singer and Singer, 1963).

The aim of this paper is to overview the technological evolution in the ceramic tile sector and its effects on product typologies through: (i) a reappraisal of composition and application of clay materials in tilemaking; (ii) the proposal of a clay classification for ceramic purposes; (iii) the review of compositional ranges for each type of ceramic tile with design criteria and guidelines for their batch formulation. Overall, the main objective is the study of the chemical–mineralogical composition and technological behavior that allows the evaluation of the applicability of the ceramic clays.

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1. Introduction

The production of ceramic tiles is growing worldwide at a rate of ~300 million m²/year and has already passed 10 billion m² in 2012 (Baraldi, 2013; Stock, 2012). Such an impressive growth implies an increase in the demand for raw materials, whose global consumption can be estimated around 230 million tons/year. The commercial success of ceramic tiles, which brought about drastic changes in raw materials and eventually gave rise to novel products (e.g., monoporosa and porcelain stoneware) and to the disappearance of classic tile types (e.g., majolica and calcareous earthenware). As a consequence, a paradigm shift occurred in the formulation of ceramic bodies and in the selection of raw materials (Becker and Brenner, 1997; Dondi, 2003; Fiori and Fabbri, 1985).

From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking. From this standpoint, classical treatises on ceramic raw materials – set up with reference to a picture of manufacturing and products already obsolete – are no longer able to describe the current market or to assess the potential of a given clay in tilemaking.

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2. Experimental approach

As a first step, a classification of ceramic tiles is outlined to introduce both terminology and basic concepts of tileaking. Criteria followed in tile classification encompass standard prescriptions and commercial issues.

Another fundamental aspect is the continuous change in technological and compositional features of ceramic tiles induced by process and product innovation. The evolution of both manufacturing technology and product types is reviewed in order to draw a picture of how the ceramic tile industry has been evolving during the last decades.

Clay materials used in the industrial practice were selected in order to get a representative picture (1040 samples) of uses, technological features, and geographic provenance. The data sources for the clays here considered are summarized in Table 1. For each clay, chemical and mineralogical composition (with rational calculation when quantitative data were not given) were considered together with particle size distribution, plasticity (Atterberg consistency limits and 

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Benlloch, 1992; Sousa and Holanda, 2005) and vitrified bodies (Beltrán et al., 1996; Lassiani Gualtieri et al., 2011; Lazar et al., 2012; Motta et al., 2001; Mukhopadhyay et al., 2009; Zanelli et al., 2011b) as well as from the industrial practice (Brusa and Bresciani, 1996; Lorici and Brusa, 1991; SACMI, 1986, 2001; Sánchez et al., 1997).

3. Ceramic tile technology

3.1. Ceramic tiles: types and classification

Ceramic tiles are classified by the ISO 13006 technical standard on the basis of water absorption: <3% (Group I), 3–10% (Group II) and >10% (Group III); groups I and II are divided in two subgroups each at the water absorption threshold of 0.5% and 6%, respectively (Fig. 1). The group code includes a letter which stands for the shaping technique: A for extrusion and B for pressing (Table 2).

In contrast, tile marketing is based on the end use: wall coverings (Group III and to a large extent iH6) and floorings (Groups I and iiH6). Along with the end use, tiles are discriminated by the body color (a different product value is usually assumed for colored and colorless bodies). The resulting terminology is somehow related to the tilemaking technology and/or the ceramic material constituting the product, so creating a patchwork of names not easy to be understood (Table 2). Fig. 1 gives a picture of tile products, stemming from the above mentioned commercial and standard issues, by contrasting body color (mostly depending on iron oxide concentration) and body

Table 1

Data sources of selected clay raw materials used in tile manufacturing.

<table>
<thead>
<tr>
<th>Country</th>
<th>No. of Data sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Italy</td>
<td>140</td>
</tr>
<tr>
<td>Brazil</td>
<td>127</td>
</tr>
<tr>
<td>Spain and Portugal</td>
<td>105</td>
</tr>
<tr>
<td>Turkey</td>
<td>83</td>
</tr>
<tr>
<td>India, Bangladesh, Pakistan and Sri Lanka</td>
<td>68</td>
</tr>
<tr>
<td>Germany</td>
<td>65</td>
</tr>
<tr>
<td>Africa</td>
<td>60</td>
</tr>
<tr>
<td>Poland, Slovakia, Czech Republic and Baltic States</td>
<td>46</td>
</tr>
<tr>
<td>Argentina</td>
<td>44</td>
</tr>
<tr>
<td>Balkan countries</td>
<td>37</td>
</tr>
<tr>
<td>France and United Kingdom</td>
<td>37</td>
</tr>
<tr>
<td>Southeastern Asia</td>
<td>35</td>
</tr>
<tr>
<td>Middle East</td>
<td>32</td>
</tr>
<tr>
<td>Russia, Belarus and Central Asia</td>
<td>26</td>
</tr>
<tr>
<td>China</td>
<td>25</td>
</tr>
<tr>
<td>other Latino-American countries</td>
<td>22</td>
</tr>
<tr>
<td>USA and Canada</td>
<td>21</td>
</tr>
<tr>
<td>Korea and Japan</td>
<td>8</td>
</tr>
</tbody>
</table>

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3.3. Evolution of ceramic bodies with technological innovation

Technological innovation has strongly affected the use of raw materials, thus a look at the evolution of ceramic tile technology is fundamental to fully understand the changes occurred in bodies formulation along the last 60 years. Product and process innovation can be perceived through the historical evolution of ceramic tiles, mainly based on data from the Sassuolo district in Italy, that is leading the technological progress in this field (Fig. 3) and the Castellón district in Spain, besides some time lags (Corma, 2008).

As a matter of fact, after the World War II a few types of ceramic tiles were on the market (Singer and Singer, 1963): essentially porous and glazed wall tiles (white body: calcareous earthenware; red body: majolica) while floor tiles were unglazed products mostly destined to industrial and outdoor applications: stoneware in its variants (red or white) manufactured by extrusion (klinker, rustic cotto) or dry pressing (red stoneware and fine stoneware). The main product innovation during the 1960s was the development of cottoforte, a glazed porous tile suitable for floorings, which switched the production towards floor tiles. The harsh energetic crisis during the 1970s compelled the ceramic industry to convert its process to a lower energy consumption, fostering the advent of fast firing in roller kilns, that turned step by step the whole tilemaking cycle into a new technology (involving wet milling > spray drying > dry pressing > fast dying and firing).

Such a novel technology, besides being much more flexible and efficient from the energetic point of view, proved to be unable to process the classic body formulations (i.e., majolica, earthenware and stoneware) thus imposing drastic changes to batch compositions. This eventually gave rise, through an empirical approach, to new products: monoporosa (manufactured by fast single fire) and then birapida (by fast double fire) took the place of majolica or earthenware and are now dominating the field of porous tiles. As red monoporosa/birapida derived from majolica, white birapida arose from calcareous earthenware but, curiously enough, white monoporosa was developed starting from stoneware formulations.

The evolution of floor tiles was more complicated (Reh, 1991): first a single-fired glazed red stoneware was achieved by modifying unglazed stoneware and cottoforte batches (and it is still the reference product for semi-vitrified or vitrified red bodies). As the use of ball clays, instead of local red-firing clays, ensured several advantages, a shift to white bodies occurred during the 1980s (Bertolani et al., 1986). By this way, a single-fired glazed white stoneware was developed, starting from (e.g. dieless pressing) entered in use especially focused on low thickness and large size, e.g. 3x1 m slabs 3 mm thick (#13). Extrusion (#10) has been recently revitalized to manufacture big slabs with novel wet technology (#8).

Tile drying was converted from old-style chamber plants (#14) to vertical driers (#15) that in the last decade made progressively room for multichannel horizontal driers (#16) and even hybrid solutions, including infra-red heating (#17).

Tile glazing is still retaining conventional processes (application by bell, disk or doctor blade) that have been gradually automatized and improved, gaining in control and quality, and enriched by dry applications; the introduction of digitalized systems is envisaged. Tile decoration moved from traditional screen printing to silicon roller printing and soluble salts, till the recent spreading of ink-jet printing.

Fast firing is the trait of ceramic process that has been continuously improved by developing roller kilns (#20) that replaced tunnel furnaces (#18) and early kinds of fast firing plants, like plates or pegs kilns (#19). Roller kilns have gradually gained wider sections, turning multichannel (#21) and able to operate at higher temperatures (up to 1250 °C). Further steps go towards hybrid furnaces, as those fed by methane and electricity (#22).

3.2. Ceramic tile manufacturing

Ceramic tiles are currently manufactured by the wet or the dry route. A detailed description of tile manufacturing goes beyond the aims of the present paper. At any rate, a short outline of technology and its evolution is given hereafter (some relevant features are reported in Table 2) with reference to the five basic steps (Various Authors, 2000–2008):

1) **body preparation** involving wet ball milling or dry grinding of raw materials and powder agglomeration by spray drying (wet route) or granulation (dry route);
2) **tile shaping** mostly by dry pressing, but also extrusion is used;
3) **tile drying** by fast cycles in vertical or horizontal driers;
4) **tile glazing and decoration** by a large set of technological solutions;
5) **tile firing** by fast cycles in roller kilns (rarely chamber or tunnel furnaces).

Additional steps can be present, like end-of-line treatments (e.g., tile polishing, cutting or functionalization), while others may be shifted along the flow-chain (e.g., decoration can be performed during shaping).

A key-point is the technological innovation that has deeply changed each processing step in the last six decades, as it can be appreciated in Fig. 2:

**Body preparation** has been since long time improving starting by the introduction of the wet route: replacing to a large extent conventional hammer mills (#1 in Fig. 2) and granulation (#6) by spray driers (#7) and ball mills with upgrading from discontinuous (#2) to continuous (#3) then to modular mills (#4). Significant improvements has been recently achieved in the dry route too, by developing versatile and more efficient roller and pendular mills (#5) as well as by granulation systems of new generation (#9).

**Tile shaping** gained a great advantage by the adoption of hydraulic presses (#12) instead of mechanical ones (#11); the former have been continuously improved, getting more powerful and reliable machines able to produce even large size slabs. Novel shaping technologies

![Fig. 1. Typologies of ceramic tiles (acronyms from Table 2) according to body color (mostly depending on the iron oxide content) and compactness (expressed by water absorption) and their classification in agreement with ISO 13006 standard.](http://dx.doi.org/10.1016/j.clay.2014.01.013)
fine stoneware formulations, turning to be the leading product in the 1990s. In the same period, a new floor tile type was launched: the porcelain stoneware (Sánchez et al., 2010). Thanks to its outstanding technical performances, it has rapidly got market shares to become now likely the most important tile product worldwide. Such a commercial success drew the implementation of the whole manufacturing route, providing substantial improvements in body preparation, shaping, thermal cycles, end-of-line treatments and particularly decoration. Porcelain stoneware, initially an unglazed floor tile for heavy traffic applications, has progressively gained aesthetic value by a wide range of decoration techniques with the creation of glazed porcelain stoneware and special body types (e.g., polished, superwhite, translucent).

4. Ceramic clays: composition and classification

The use of clays in tile manufacturing, hence their commercial classification, depends on the technological and appearance requirements of each kind of ceramic body: firstly the color after firing and secondly the behavior during the tilemaking process, involving properties like slip viscosity, plasticity, drying sensitivity, fusibility, pore-forming ability and so on, which are strictly connected with clay mineralogy and particle size distribution (Bal and Fiederling-Kapteinat, 2007; Dondi, 1999; Dondi et al., 2003; Stentiford, 2005).

First of all, ceramic bodies are distinguished in light-firing (from white to light brown) and dark-firing (from pink to dark brown) on the basis of color after firing. This color depends essentially on the iron oxide content, even if a certain role is played by further components (as TiO₂ and CaO) that may turn the color to yellowish or pinkish shades. Overall, clays used in light-firing and dark-firing bodies are fairly well discriminated by a Fe₂O₃ content of approximately 3 wt.

Table 2

<table>
<thead>
<tr>
<th>Body type</th>
<th>Water absorption % wt.</th>
<th>Class (ISO 13006)</th>
<th>Tile type (commercial name)</th>
<th>Tile features</th>
<th>Tile features</th>
<th>Minimum modulus of rupture MPa</th>
<th>Resistance to deep abrasion mm³</th>
<th>Typical firing schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>POROUS</td>
<td>&gt;10</td>
<td>BII All</td>
<td>Majolica</td>
<td>D P G</td>
<td>MAJ</td>
<td>15</td>
<td>no prescription (BII)</td>
<td>960–1050 (biscuit)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calcareous earthenware</td>
<td>L P G</td>
<td>CEW</td>
<td>≤2365 (All)</td>
<td>940–980 (glaze)</td>
<td>1040–1060 (biscuit)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Red birapida</td>
<td>D P G</td>
<td>RBR</td>
<td></td>
<td>960–980 (glaze)</td>
<td>1030–1140 (biscuit)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>White birapida</td>
<td>L P G</td>
<td>WBR</td>
<td></td>
<td>1030–1150 (glaze)</td>
<td>1100–1150 (biscuit &amp; glaze)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Red monoporosa</td>
<td>D P G</td>
<td>RMP</td>
<td></td>
<td>1070–1100</td>
<td>1100–1140</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>White monoporosa</td>
<td>L P G</td>
<td>WMP</td>
<td></td>
<td>1120–1160</td>
<td>40–50 min</td>
</tr>
<tr>
<td>SEMI POROUS</td>
<td>6–10</td>
<td>BIIₗₐ BIIₐ</td>
<td>Rustic cotto</td>
<td>D E(P) U</td>
<td>RUS</td>
<td>17.5</td>
<td>≤649</td>
<td>950–1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cottonforte</td>
<td>D P G</td>
<td>CFO</td>
<td>18</td>
<td>≤540</td>
<td>980–1060 (biscuit)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Red monoporosa</td>
<td>D P G</td>
<td>RMP</td>
<td></td>
<td>960–980 (glaze)</td>
<td>1120–1160</td>
</tr>
<tr>
<td>SEMI VITRIFIED</td>
<td>3–6</td>
<td>BIIₗₐ BIIₐ</td>
<td>Red stoneware</td>
<td>D P G</td>
<td>GRS</td>
<td>18 (BIIₗₐ)</td>
<td>≤540 (BIIₗₐ)</td>
<td>950–1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Klinker</td>
<td>L E U</td>
<td>KKL</td>
<td>23</td>
<td>≤275</td>
<td>1100–1200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>White stoneware</td>
<td>D P U</td>
<td>URS</td>
<td>30</td>
<td>≤175</td>
<td>980–1000</td>
</tr>
<tr>
<td>Highly VITRIFIED</td>
<td>&lt;0.5</td>
<td>BIIₗₐ BIIₐ</td>
<td>Porcelain stoneware</td>
<td>L P G</td>
<td>GWS</td>
<td>30</td>
<td>≤175</td>
<td>1170–1200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Porcelain stoneware</td>
<td>L P G</td>
<td>GPS</td>
<td>35</td>
<td>≤175</td>
<td>1190–1220</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L P(E) U</td>
<td>UPS</td>
<td>1200–1230</td>
<td>45–75 min</td>
<td></td>
</tr>
</tbody>
</table>


4.1. Light-firing clays (LFC)

Light-firing clays encompass several commercial types going under the general terms of kaolin and ball clay (including pyrophyllite and to some extent bentonite) each referring to a wide range of mineralogical and granulometric characteristics. From the mineralogical point of view, they basically consist of phyllosilicates (mostly kaolinite) and silica phases (quartz and exceptionally cristobalite, tridymite andopal), although further components (feldspars, iron and aluminum oxhydroxides, organic matter) may be present. Among clay minerals, along with kaolinite, also illite, interstratified I/S, halloysite, smectite, pyrophyllite, sericite, dickite, interstratified K/S, vermiculite and chlorite can be found in decreasing order of frequency.

Besides the general distinction between kaolin and ball clay (Harvey and Murray, 1997) these terms are used quite freely for commercial purposes regardless genetic, compositional or technological features (ICERS, 1995–2010). In practice, it often happens that similar raw materials be termed as “kaolin” or “ball clay” depending on the end-use; other clays, very different in composition and particle size, may be classified under the same term. For this reason, we propose a classification based on the following criteria: iron oxide content, amount of kaolinite group minerals (kaolinite, halloysite, dickite); percentage of quartz and other phyllosilicates (particularly pyrophyllite and expandable clay minerals: smectite + interstratified I/S); particle size distribution and plasticity (Atterberg consistency limits and Methylene Blue Index). By this way, low iron oxide clays (hence light-colored after firing) are distinguished by the amount of kaolinite group minerals into the following classes (Figs. 5 and 6):

>75% High-grade Kaolins (HK), characterized by high to very high amount of kaolinite and/or halloysite, may contain low amounts of illite-mica, Al-oxhydroxides and non plastic
components (quartz, feldspars, rock fragments, titanium dioxide) each below 15%.

50–75% Low-grade Kaolins (LK), besides predominantly kaolinitic, contain from low to significant amounts of illite and/or interstratified I/S along with an always important non plastic portion, made up of quartz, feldspars, etc.

25–75% Ball Clays (BC) have an amount of kaolinite group minerals analogous to low-grade kaolins (although it can be below 50% in case of illite-rich materials). As a matter of fact, the overall mineralogical composition of BC overlaps to a large extent those of kaolins (Fig. 6). The distinction between low-grade kaolins and ball clays is here proposed in terms of plasticity (Fig. 5). Ball clays are distinguished from raw kaolins (when kaolinite content is <50%) by their large particle fraction below 2 μm, at least 40% by weight.

25–50% Raw Kaolins (RK) are basically deeply kaolinized parent rocks (in case of primary deposits) that contain a lot of non plastic components (particularly rock fragments, quartz, feldspars and mica). In any case, the amount of phyllosilicates must be high enough to bestow a sufficient, although low, plasticity on the raw kaolin to act as a clay material. Kaolinitic Loams (KL) are sedimentary deposits where kaolinite is admixed with an abundant non plastic fraction (mainly quartz) frequently accompanied by other clay minerals (smectite, interstratified I/S, illite, chlorite). Both raw kaolins and kaolinitic loams are characterized by a coarse-grained particle size distribution with often a significant sandy fraction (>25% over 63 μm).

<25% Light-firing clays poor in kaolinite and containing more than 20% of pyrophyllite or smectite constitute special cases, being classified as Pyrophyllitic Clays (PC) or White Bentonites (WB) respectively.

4.1.1. High-grade Kaolins (HK)

In ceramic tile manufacturing, high-grade kaolins are easily dispersable in water, but difficult to press and highly refractory, enhancing the formation of mullite and whiter shades during firing. More refractory terms often need to be milled in order to exhibit a plastic behavior, so presenting analogies with flint clays (Keller, 1968). HK are typically used in low amounts: a few percent in glazes and engobes (to thicken and stabilize suspensions) and no more than
10–15% in porous and vitrified bodies (unglazed porcelain stoneware and white birapida). Examples of HK used in tilemaking are kaolins from Cornwall, UK (Bristow, 1993; Scott et al., 1996) and Bayern, Germany (Keck, 1991; Kitagawa and Köster, 1991) or some grades from Kütahya, Turkey (Kadir et al., 2011; Yaniik, 2011).

4.1.2. Low-grade kaolins (LK)
The behavior of low-grade kaolins in the ceramic cycle is influenced by components associated to kaolinite in the plastic and non plastic fractions. For instance, the technological performance of the materials higher in kaolinite and poor in feldspars and expandable clay minerals does not substantially differ from that of high-grade kaolins, although their use is restricted to engobes and glazes. Higher in kaolinite and poor in feldspars and expandable clay minerals, their use is restricted to vitrified and porous bodies (usually in percentages larger than HK) being generally not utilized in engobes and glazes. When the amount of kaolinite group minerals approaches 50%, the technological behavior is clearly different from that of HK, due to the increased non plastic fraction, implying lower plasticity and confirming difficulties in pressing and sintering. However, these limits can be to some extent overcome by the occurrence of feldspars (enhancing fusibility and fostering sintering) and expandable clay minerals (improving plasticity). At any rate, the LK class defines clays with a rather low plasticity (MBI< 7.5). Examples of LK used in tilemaking are kaolins from Santa Severa, Italy (Costa et al., 1996) or Sinitsa and Dedovka, Belarus (Levitskii et al., 1997; Sergievich et al., 2012) and some grades from Muang Ranong, Thailand (Bordeepong et al., 2012; Worasith et al., 2011).

4.1.3. Raw kaolins (RK)
The utilization of raw kaolins in tilemaking is not straightforward, so it is frequently disregarded. As a matter of fact, raw kaolins cannot fulfill ordinary requirements for ceramic clays, especially due to their poor plasticity. However, RK may play as a sort of mix, thanks to comparable amounts of kaolinite, quartz and flux (feldspars, rock fragments) whose technological behavior has to be balanced by the other clays and fluxes making up the body. The addition of raw kaolin turns to be useful particularly when the distance from mine to tile factory is short, so permitting to have a low cost. Examples of RK used in tilemaking are raw materials from Romana (Ligas et al. 1997) and Piloni di Torniella, Italy (Bertolani and Loschi Ghittoni, 1989; Viti et al., 2007) or Michoacán, Mexico (Guillén et al., 2012).

4.1.4. Kaolinitic loams (KL)
Some sedimentary deposits utilized by the ceramic industry contain, as the raw kaolins, an abundant non plastic fraction, mainly consisting of quartz with some feldspars and sometimes carbonates. These clay materials are here named kaolinitic loams due to their coarse grain size distribution, strongly affecting their technological behavior. This can be described as a compromise between coarse grain size and relatively high plasticity, due to the frequent occurrence of expandable clay minerals together with kaolinite. Such a peculiar composition turns KL a rather versatile raw material, that can be addressed to vitrified and porous bodies up to 20–25%. Examples of KL used in tilemaking are Italian clays from Lozzolo, Piedmont (Fiori and Fabri, 1987) and Florinas, Sardinia (Danasino and Di Primio, 1995).

4.1.5. Ball clays (BC)
According to the classical definition “Ball clay is a fine-grained, highly plastic, mainly kaolinitic sedimentary clay, the higher grades of which fire to a white or near white colour” (Wilson, 1998). In reality, in ceramic tile production such a definition is stretched to cover a proper (or even a just acceptable) behavior during wet milling, pressing and sintering, regardless of compositional features. As a consequence, an outstanding range of compositions and technological properties goes under the commercial term of “ball clay” (ICerS, 1995–2010). In practice, BC used in tilemaking plot over almost the entire Kaolinite-Illite-Quartz + Feldspar ternary diagram (Fig. 6) implying wide ranges of kaolinite (20–80%), illite (0–60%), quartz (0–60%) and feldspars (0–30%) concentrations. Expandable clay minerals (mostly interstratified illite-smectite and sometimes smectite) are common components that can reach 25% and, although they are not always present, may affect significantly plasticity and behavior during pressing and drying. Other components include iron oxyhydroxides (usually below 2%, or if slightly higher amounts may be tolerated) and organic or carbonaceous matter (commonly in the 0.1–0.7% range). Further minerals (e.g., pyrophyllite, interstratified K/S, chlorite, gibbsite, carbonates) are sometimes present in low amount. Particle size distribution is in most cases fine-grained with the clay fraction over 50% and frequently over 75%. However, some raw materials going under the term “ball clay” exhibit a rather coarse grain size with the silt fraction over 50% (Fig. 7). Overall, these large sets of mineralogical and granulometric data reflect into wide ranges of technological properties of BC, entailing plasticity and behavior during compaction, drying and firing. Ball clays are characterized by a wide range of MBl₄—going from 8 to 40 meq/100 g (Dondi

Fig. 5. Classification of light-firing clays according to their amount of kaolinite group minerals and clay fraction as well as their Methylene Blue Index at pH ~ 4 (MBI) or Atterberg Plastic Index.
et al., 2003, 2008; Wilson, 1998)–with on the whole higher values with respect to LK. This picture allows to classify LFC according to the technological performance (Fig. 5): low plasticity clays (MBI < 7.5; typically kaolins: HK, LK, RK); medium plasticity clays (7.5 < MBI < 12; BC1); high plasticity clays (12 < MBI < 16; BC2); and very high plasticity clays (16 < MBI < 30; BC3 and some WB); extremely high plasticity occurs only in bentonites among ceramic raw materials. These limits are traceable to the technological behavior in tilemaking and differ from established reference schemes (Polidori, 2003 and references therein). There are many examples of BC used in tilemaking (McCuistion and Wilson, 2006): clays from Westerwald, Germany (Marx and Hennicke, 1986; Petrick et al., 2011); Donbass, Ukraine (Fiederling-Kapteinat et al., 2000; Naimo et al., 2000); Santa Cruz, Argentina (Domínguez et al., 2008).

4.1.6. Pyrophyllitic clays (PC)

Some clay materials used in ceramic tile production are characterized by the occurrence of pyrophyllite, from a few percent up to 80% wt. Since pyrophyllite has a different technological behavior with respect to kaolinite, it is convenient to classify as Pyrophyllitic Clays (PC) the raw materials with a significant amount of pyrophyllite (>20%) as they present commonly lower loss on ignition, easier compaction, and lower refractoriness with respect to kaolins (Mukhopadhyay et al., 2009; Sánchez-Soto and Pérez Rodríguez, 1998). PC are usually claystones of different origin that, along with pyrophyllite, contain quartz, feldspars and often kaolinite and/or illite or sericite. Pyrophyllitic clays can replace BC in many applications and are used in tilemaking especially in India (Das and Mohanty, 2009; Mukhopadhyay et al., 2010) and Argentina (Dristas and Frisciale, 2003; Zalba, 1979), being roseki in Japan and Korea (Higashi, 2000; Matsuda et al., 1981).

4.1.7. White bentonites (WB)

Clays with a high amount of smectite (frequently over 50% wt, Fig. 6) and a relatively low iron content (Fe₂O₃ at max 6%, but preferably below 2%) are used in tilemaking as additives to enhance plasticity of too lean bodies. This kind of clay materials is commonly referred to as White Bentonites, although the firing color of the terms richer in iron is rather dark. Quite complex mineralogical assemblages are common: smectite together with other phyllosilicates (interstratified I/S and less frequently kaolinite or illite), silica phases (quartz, cristobalite, tridymite, opal), feldspars, volcanic glass and rock fragments. The use of WB in tilemaking is substantially addressed to increase the mechanical strength of unfired bodies, though their maximum tolerable amount is constrained by rheological properties during wet milling and spray-drying (smectite induces a sharp increase of slip viscosity and thixotropy) as well as by drying sensitivity (Andreola et al., 2009). These technological constraints make it preferable to have WB with not too much smectite and particularly with a moderate activity.

Fig. 6. Mineralogical composition of light-firing clays for ceramic tiles.

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4.2. Dark-firing clays (DFC)

Red-firing clays are commonly gathered in a single category, so implying a very wide variation range in terms of mineralogical composition, particle size distribution and technological behavior. From the mineralogical point of view, DFC consist predominantly of phyllosilicates (from 35% to over 90%) associated with quartz (up to 50%), carbonates (up to 50%), feldspars and rock fragments (up to 40%), iron oxyhydroxides (up to 15%), and minor components depending on the origin of clay deposits (organic matter, sulfides, sulfates, etc.). Particle size distribution can span from silty clays to clay silts and loams, with the <2 μm fraction ranging from 20 wt.% to 80 wt.%.

However, the main parameters considered in the industrial practice are:

- the occurrence of carbonates, which play a complex role during firing, entailing the formation of a small-sized porosity, as of new crystalline phases (e.g., plagioclase, pyroxene, and melilitc) controlling firing shrinkage, thermal and moisture expansion, and making the production of net-shaped tiles feasible (Billi et al., 1992; Dagounaki et al., 2008).

- The degree of lithification may affect, depending on the milling process, both particle size distribution and plasticity, therefore the behavior during shaping and sintering. A strongly lithified material (e.g., a shale) may change significantly its ceramic behavior according to its grain size distribution, being classified as clay or loam depending on the degree of milling (Alló et al., 1997).

- The so-called ‘fusibility’, or more properly the critical temperature at which sintering begins to run by viscous flow of the amorphous phase formed at high temperature. It discriminates easily sintered (self-sintering or vitrifying) clays from more refractory ones.

The criteria followed in the classification of DFC are: iron oxide content (the 3% Fe2O3 threshold already mentioned for LFC), amount of carbonates, coarse-grained fraction (>63 μm), amount and type of phyllosilicates (the terms richer in expandable clay minerals are not suitable for the wet route), plasticity by Atterberg consistency limits (MBI values are just seldom available for DFC). Overall, these criteria allow to distinguish the iron-rich clays in the following classes (Fig. 8):

4.2.1. Marly Clays (MC) and Carbonatic Clays (CC)

Calcite and dolomite are common constituents of many ceramic clay materials and their amount spans from absent to over 40%. A lower threshold is here proposed at 10% carbonates (calcite + dolomite) to define the field of marly clays. Although to a certain extent arbitrary, this threshold actually discriminates clay materials whose main use is in wall tiles. However, in the body formulation for wall tiles, particularly in the case of monoporosa technology, the maximum amount of a given clay depends primarily on its content in calcite and dolomite: the lower the carbonates percentage, the higher the amount of clay that can be used. For this reason, it is proposed also an upper threshold at 30% of carbonates that define carbonatic clays whose use is generally restricted as a minor component in monoporosa and especially birapida tiles. MC and CC are overall characterized by the most complex mineralogical composition among ceramic clays, where different types of phyllosilicates (commonly illite, chlorite, smectite plus minor kaolinite and interstratified terms), carbonates and quartz are all present in significant amounts (Fig. 9). From the granulometric viewpoint, MC range from silty clays to clay silts with a low sandy fraction (Fig. 10). Typical carbonate-bearing clays used in tilemaking are from Castellón, Spain: for example the Mas Vell (MC) and Araya (CC) clays (Bastida and Beltrán, 1986; Meseguer et al., 2011b; Sánchez et al., 1997) or the Ranzano Fm in Sassuolo for MC (Dondi, 1999).

4.2.2. Red Clays (RC)

Red clays (RC) practically include every iron-rich clay material with Fe2O3 over 3%, carbonates below 10% and a coarse-grained fraction below 25%. These thresholds define an extremely wide space, both in terms of mineralogical composition and particle size distribution, that as a consequence reflects into different technological behaviors. The phyllosilicates-to-quartz + feldspars ratio can vary greatly, implying that RC can contain a non plastic portion up to 70% (Fig. 9) spread in different way over the silty and sandy fractions (Fig. 10). Furthermore, RC are commonly complex mixtures where 3 to 5 groups of clay minerals (kaolinite, illite, smectite, interstratified terms and chlorite, sometimes pyrophyllite and vermiculite) coexist in the same raw material (Fig. 9). Besides this complicated compositional picture, no distinctions are practiced in the industrial production beyond that of

Fig. 7. Particle size distribution of light-firing clays for ceramic tiles.
Red Clays. In order to fill this gap, a classification is here proposed in terms of phyllosilicate assemblages (Fig. 8):

- predominantly *kaolinitic red clays* (RC1) where kaolinite group minerals represent over 50% of the total of phyllosilicates; the amount of chlorite or expandable clay minerals is always below 20%.
- Prevalently *illitic red clays* (RC2) where illite-mica terms are over 50% of phyllosilicates and the amount of smectite, interstratified IS and chlorite is within 20%.
- Mixed types like *illite-chlorite red clays* or *illite-smectite red clays* (RC3) where the amount of chlorite and/or expandable clay minerals associated to illite is over 20% of the total of phyllosilicates.

Different technological behaviors are expected for these red clay types: the RC1 grades richer in kaolinite are rather plastic and refractory (somehow approaching the definition of fireclay) besides significant amounts of sandy fraction are frequent. Illite-rich RC2 terms are in many cases silty clays, quite fusible but with a poor to moderate plasticity. R3 are mostly silty clays, highly fusible, with moderate plasticity in case of chlorite-rich terms (Carretero et al., 2002) to high plasticity of the smectite-rich grades. For all types, the plastic behavior is also heavily affected by the amount of non plastic component.

Examples of red clays used in tilemaking are those from Neuquén, Argentina, for RC1 (Cravero et al., 1997); Villar and Chulilla clays from Castellón, Spain, for RC2 (Bastida, 1982a, 1982b; Bastida and Beltrán, 1986); and for RC3 the Corumbataí Fm, Brazil (Christofoletti and Moreno, 2004; Motta et al., 2005) and various red shales from the Sassuolo district in Italy (Dondi, 1999; Fiori, 1996).

### 4.2.3. Red Loams (RL)

Red loams (RL) represent substantially a special case of red or marly clays with an abundant coarse-grained fraction (over 25% >63 μm, Fig. 10). This sandy component typically consists of quartz, feldspars and rock fragments. The clay fraction is frequently a mix of illite, kaolinite and chlorite, with expandable clay minerals sometimes present. Such a peculiar composition turns RL especially suitable for extruded products and not surprisingly they are extensively used in the manufacturing of heavy-clay products (Fabbri and Dondi, 1995). In tilemaking, RL are typically utilized in the manufacture of rustic tiles, but in proper amounts they may be added practically to every type of red tile bodies in total or partial replacement of filler (Kayaci et al., 2010). Red loams are exploited, for example, in Tuscany and Piedmont, Italy (Bertolani and Loschi Ghittoni, 1986b, 1990; Malesani, 1992) as well as in the Teruel basin, Spain (Bastida et al., 2006; García-Tomás et al., 1996).

![Fig. 8. Classification of dark-firing clays according to their coarse-grained fraction, amount of carbonates and clay minerals.](image)

5. Ceramic bodies: formulation and design criteria

In the design of body recipes for ceramic tiles, four basic ingredients are necessary:

- Clay, stabilizing suspensions (in the wet route), ensuring the plasticity necessary for shaping, and bestowing mechanical strength on unfired tiles; during firing clay acts as flux (e.g., illite) or mullite precursor (e.g., kaolinite).
- Flux, forming a liquid phase at high temperature that allows to densify the ceramic body by a viscous flow; feldspars are the typical flux, but sericite, feldspathoids, and further raw materials are utilized too.
- Filler, providing a coarse-grained structure (so-called skeleton) contrasting deformations during drying and firing; the most common filler is quartz sand, though chamotte or other sand types are sometimes used.
- Additives, like a *pore-forming agent* which develops porosity during firing and fosters sintering by surface diffusion (role frequently carried out by carbonates); other additives are pigments, opacifiers and sintering promoters.

Technological innovation has been increasing the flexibility of tilemaking processes, so allowing the preparation of ever more complex batches, that usually include up to a dozen different raw materials. It is common in the industrial practice to use more than one source of clay, flux and filler in order to dump any fluctuation in composition and technological properties. Body formulation is focused on both technological behavior and technical performance of finished products, thus it is strictly connected with key properties of each typology of ceramic tiles. About the behavior during the tilemaking process, the following key properties are particularly stressed:

- Rheological properties of slips, in the wet route, that affect dramatically the efficiency of milling and spray drying (Andreola et al., 2009);
- Bending strength of unfired tiles that must be high enough (usually >4 MPa) to withstand wet glazing and mechanical stress of screen printing (this latter requirement can be relaxed in case of non contact decoration, e.g. by inkjet printing);
- Porosity and linear shrinkage that must match the target after a proper firing schedule;
- Absence of bulk or surface defects (black core, planarity, glaze appearance, etc.).

The technical performances refer to the prescriptions of the international standard ISO 13006 for each tile typology; particularly relevant are the following:

- Water absorption to fit the window of acceptance for each class (Fig. 1);
- Modulus of rupture and resistance to deep abrasion according to each class (Table 2);
- Coefficient of thermal expansion (CTE) that ensures the body-glaze thermodilatometric matching, so preventing crazing defects;
- Resistance to moisture expansion in order to prevent damages to floorings and wallings (Hall and Hoff, 2012).

Furthermore, the body color after firing is an important commercial aspect.

The criteria of body formulation will be outlined, for simplicity sake, by identifying three broad categories: porous bodies (WBR, WMP, RBR and RMP typologies); semi-vitrified and vitrified red bodies (GRS); vitrified light-firing bodies (GWS, GPS, UPS); roughly corresponding to BIIl, BII and BI classes of the ISO 13006 standard, respectively. However, account must be taken that multipurpose bodies are sometimes designed by the industry: a single batch can be formulated to produce two different typologies (e.g., BIIl or BII, BII or BII) just changing the processing parameters (Brusa and Bresciani, 1996; Dondi et al., 2001; Kara et al., 2006).
5.1. Porous bodies

Porous bodies (water absorption > 10%) are addressed to wall tiles that are manufactured by either the monoporosa technology (fast single firing) or the birapida technology (fast double firing) for both colored bodies (RMP and RBR) and white bodies (WMP and WBR). Industrial firing schedules are typically running at 1000–1140 °C of maximum temperature with 30–45 minutes cold-to-cold.

Porous bodies are designed to get net shape tiles, whose final dimensions are the same of the mold used for pressing. As a consequence, drying and firing shrinkages must be very low, never exceeding 1 cm/m. Porosity is constrained by the minimum bending strength required, that is 15 MPa. As porous bodies are always glazed, special care is needed to ensure the body-glaze thermodilatometric matching, by controlling both CTE (α20–400 °C typically in the 6.5–8.0 MK–1 range) and moisture expansion (recommended <0.1%).

This overall target is easier accomplished with calcium-rich bodies that promoting the formation of Ca–Mg silicates (plagioclase, pyroxene, mellite, etc) during firing result stronger and more stable to moisture than low calcium bodies even with a high porosity. A detailed description of phase transformations occurring during the thermal treatment of carbonatic clays and porous bodies can be found in the literature (Dondi et al., 1995a, 1998, 1999a, 1999b; González-García et al., 1990; Hajjaji and Mezouari, 2011; Jordán et al., 1999, 2001, 2008, 2009; Kacim and Hajjaji, 2003; Serra et al., 2013; Trindade et al., 2010).

There are three main routes to design proper porous bodies (Tables 3 and 4):

P1 by using carbonate-bearing clays (MC and CC);
P2 by adding calcite or dolomite to the batch;
P3 by introducing Ca or Ca–Mg raw materials different from carbonates.

Route P1 is commonly adopted for red bodies; only when no suitable carbonate-bearing clay is available, route P2 is followed to get RMP and RBR tiles. White bodies are always manufactured by route P2, but when neither calcite nor dolomite are available (or large size, high quality WMP tiles have to be produced without carbonates). In these cases, route 3 opens a wide range of solutions in terms of alkaline-earth oxides-bearing raw materials: wollastonite, diopside, talc, synthetic silicates (including frits and glass–ceramic systems).

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In any case, the expected color of fired body is white for WMP and especially WBR (Fe₂O₃ of the batch is usually < 1%, at most 2% wt dry-basis). Although there is no emphasis on color for RMP and RBR, the Fe₂O₃ content of fired bodies is usually from 4 to 6% (at maximum 8% wt). Porous tiles produced by the wet route (particularly white bodies as well as many red monoporosa plants) preclude the use of raw materials with abundant expandable clay minerals (BC3 and some RC3 and MC cannot be utilized as main components).

5.1.1. Monoporosa technology

Monoporosa technology allows to fire at the same time body and glaze, with conspicuous advantages in terms of cost and productivity. However, calcite thermal decomposition occurs, due to the fast firing cycle, at rather high temperatures and may overlap glaze melting; if CO₂ released from CaCO₃ breakdown passes through a melted glaze, it will cause defects (pinholes). In order to prevent pinholes, the kinetics of calcite (or dolomite) breakdown has to be accelerated by: (i) reducing the carbonate particle size, (ii) fostering the gas permeability (lower bulk density of unfired tile by lower load at the press) and (iii) limiting the carbonate amount of the batch. For this purpose, carbonates in monoporosa bodies are constrained to 7–12 wt.% (at most 15%). It implies that MC have to be within ~60% of RMP batches (much less in the case of CC) with some RC together with filler or RL to control gas permeability (Kayaci et al., 2010). Filler is privileged in Italian-style bodies (Fig. 11 and RMP1-2 in Table 4) while RL is preferred in Spanish-style batches (Fig. 11 and RMP3). WMP bodies were derived from stoneware batches and for this reason their formulation may contain low-grade kaolins and kaolinitic loams, along with ball clays or pyrophyllitic clays, together with significant amounts of filler and fluxes (Fig. 12 and WMP3-4 in Table 3).

5.1.2. Birapida technology

Birapida technology was developed to overcome the technological constraints of monoporosa, making simpler – besides the additional cost of a second fire – the production of porous tiles. As the body is first fired without glaze, the amount of carbonates in the batch can be higher than 12–15%, although percentages over 20% (that were common in the traditional majolica and calcareous earthenware industry) are not recommended. RBR batches came from majolica formulations: they are based on 60–80% marly clays corrected by some red clays, with little filler or RL as there is no gas permeability requirement. If CC are utilized, a higher amount of RC is necessary. The main distinction between RBR and RMP bodies, in fact, is the higher amount of MC and the often lower percentages of filler and flux.
(Fig. 11). On the other hand, WBR derived from calcareous earthenware batches, so still make use of kaolins, large amounts of filler and sometimes fluxes. WBR bodies exhibit both a higher kaolin-to-ball clay ratio and larger amounts of filler with respect to WMP batches (Fig. 12). Pyrophyllite-bearing batches are often fluxed by wollastonite without carbonates (e.g. WBR4 in Table 3).

5.2. Vitriﬁed and semi-vitriﬁed red bodies

Vitrified and semi-vitriﬁed red-ﬁring bodies are utilized for ﬂoor tiles that fall in the Blp and Bllp classes (water absorption 0.5–3% and 3–6%, respectively); semi-porous bodies with water absorption 6–10% (Bllp) are addressed, along with ﬂooring, to wall coverings. This large set of products goes under the commercial name of red stoneware with its variants (glazed, unglazed, rustic) regardless of the Blp, Bllp or Bllp classiﬁcation. Red stoneware is manufactured by fast single ﬁring at 1120–1180 °C of maximum temperature in 20 to 50 min cold-to-cold. Sometimes rustic tiles are processed by slow single ﬁring of heavy-clay industry (Table 2). Red stoneware is nowadays produced by the dry route more frequently than by the wet route (Motta et al., 2004). It is almost always glazed; only rustic tiles and some low porosity tiles for outdoor applications (Blp) are unglazed.

Mineralogical transformations occurring during the ﬁring of low porosity red bodies are generally simpler than those of carbonate-bearing batches. In fact, they essentially entail the breakdown of clay minerals (with formation of new crystalline phases: mullite and less frequently sanidine, spinel, olivine) and feldspars (with development of a more or less abundant vitreous phase). Hematite crystalization from Fe-oxhydroxides is a distinctive feature of these bodies (Hajjaji et al., 2002; Jordán et al., 2008; Khalfaoui and Hajjaji, 2009; Pardo et al., 2011; Trindade et al., 2010).

The main concern in the design of red stoneware bodies is to ﬁt the standard target (water absorption, mechanical strength, etc) with ﬁring schedules that must be as faster (best 40 min or less) and as colder (best 1170 °C or less) as possible. Firing shrinkage must be within 6 cm/m (Blp) or 9 cm/m (Blp) as ﬁring deformations must be kept under strict control. For this purpose it is useful to have a certain quartzous skeleton (typically 20-30%) which also helps to get the correct CTE (7–8 MK–1).

Different properties are expected for bodies processed by the wet or the dry route, beyond some convergency of requirements: e.g., highly plastic clays are tolerated in low amounts in both wet milling (as they increase the slip viscosity) and dry cycle (they are difﬁcult to moist by granulation). Generally speaking, expandable clay minerals should be avoided in the wet route (recommended ≤5% in the batch) as coarse-grained clay materials should not be utilized in the dry route (limiting particularly the silty fraction that is little affected by dry milling). Body color varies from light red to dark brown (when MnO2 is added to prevent black core) as Fe2O3 amount is usually in the 3–7% range (at maximum 9 wt.%).

The strategies of formulation differ from rustic to glazed tiles, and these latter from semi-vitriﬁed to vitriﬁed bodies. Batches for rustic tiles are simple and often entirely made up of red loam with plasticity suitable for extrusion (Fabbri and Dondi, 1995; Vieira and Monteiro, 2012); in alternative, red clays are corrected with a ﬁller (Table 4).

5.2.1. Vitriﬁed red stoneware

Vitriﬁed red stoneware was developed from the traditional unglazed stoneware by adjusting the technological behavior of red clays to the requirements of fast single ﬁring (Fig. 11). Batches were changed by introducing some ﬂux (to improve sintering kinetics) and some ﬁller (to contrast black core and pyrodeformation) in order to make it...
possible the fast firing rates (Fabbri and Fiori, 1985; Sánchez et al., 1990). Therefore, the following criteria are applied in the industry to formulate red stone ware bodies (Table 4):

- fine-grained, often plastic and refractory red clays (like kaolinitic types RC1) can be used up to 30%, as they need the addition of both flux and filler, commonly within 20% each;
- raw materials that naturally contain enough feldspars, illite and/or chlorite to be ‘self-sintering’ (like many RC2 and RC3 clays) can be used in large amounts (35–65%) being adjusted by adding filler, usually below 20%;
- red loams (RL) frequently have enough coarse-grained fraction to replace simultaneously filler and clay (when employed, their amount is 25–40%).

The flexibility in body formulation turned it possible—and in many cases necessary— to combine two or more of the above criteria, mixing different types of red clays and even different kinds of filler and flux.

5.2.2. Semi-vitrified red stone ware

Semi-vitrified red stone ware has overall a batch composition close to that of the vitrified bodies, to the point that in several cases the same body can be used to produce BII or BI tiles just modifying the firing cycle. However, BII tiles are easier to be produced, due to their higher water absorption, with bodies containing some carbonates, that can be provided by either calcite-bearing RC (which may contain up to 10% carbonates) or a minor amount of MC to be added to carbonate-free RC (i.e. the cortoforte approach, GWS in Table 4). A distinctive treat of semi-vitrified tiles is the chance to have bodies based on a single clay able to fulfill all technological requirements (feasible for the rather large window of acceptance: e.g. 6–10% water absorption). It happens for instance with some terms of the Curumbatá Fm that constitute the whole batch of the BII production in the Santa Gertrudes district, Brazil (Boschi, 2004; Masson et al., 2000; Motta et al., 2004).

5.3. Vitrified light-colored bodies

Light-colored bodies are utilized to manufacture vitrified (BIII) and highly vitrified (BIII) floor tiles that correspond to commercial types Glazed White Stone ware (GWS) and Porcelain Stone ware, respectively. All these products are manufactured by the wet route, with a few exceptions (Meliades et al., 2010). GWS bodies are typically fired at 1160–1190 °C for 35–50 min cold-to-cold to get water absorption in the 1–3% range. Porcelain stone ware tiles can be either glazed or unglazed and are usually fired at 1190–1240 °C for 50–70 min to fulfill the market requirement of water absorption ~0.1% (although standard limit is <0.5%). The outstanding innovation in porcelain stone ware technology has led to the production of large slabs (up to 360x120 cm²) as very thin (0.3 cm) to very thick (2.5 cm) tiles and their combination (large and thin slabs) by uniaxial pressing, dieless pressing, or extrusion (Raimondo et al., 2010). These large sized tiles require a special body formulation with particular care in the choice of clay raw materials and additives.

The firing transformations occurring to LFC and light-colored bodies are the subject of several studies (Aras, 2004; Bastida et al., 2006; Gualtieri, 2007; Hajjadi et al., 2008; Jordan et al., 2008; Lee et al., 2008; Zanelli et al., 2011b) also concerning their effect on the properties of tiles (Bakr, 2011; Carbajal et al., 2007; Ferrari and Gualtieri, 2006; Lassinanti Gualtieri et al., 2011; Mukhopadhyay et al., 2003, 2009, 2010).

Light-colored vitrified bodies are designed to fit the water absorption target by firing schedules achievable with roller kilns, complying all standard requirements in terms of mechanical, abrasion, frost, chemical, stain and thermal shock resistance. This objective is achieved through viscous flow sintering, whose fast densification rates make it crucial the control on firing shrinkage (recommended <7 cm/m²) and pyroplastic deformation, with most technical properties depending on the interplay of residual porosity and phase composition, especially the vitreous phase (Gualtieri, 2007; Zanelli et al., 2011b). Thus, particle size distribution is stressed, since the specific surface area created by milling is the driving force of sintering, like fluxes (sodic, potassic, alkaline-earth and their combination) are strongly concerned, as they directly affect amount and composition of the vitreous phase. Being the more refractory (and expensive) component in light-colored vitrified bodies, along with the richest in iron, clay is kept to a minimum: its role is essentially restricted to govern the technological behavior before firing. The clay contribution during firing is mainly that of mullite precursor (kaolinite, pyrophyllite) or additional flux in case of illite and interstratified IS (Lee et al., 2008). In particular, slip rheological properties (milling and spray-drying), plasticity and compressibility (pressing) and bending strength (glazing and decoration) are the key points for clay raw materials (Bougher, 1995; Dondi et al., 2008). A compromise is necessary to match the slip requirements in terms of viscosity and thixotropy ( recommending low amount of smectite and interstratified IS) with the needs of plasticity and strength (satisfied by a relatively high percentage of expandable clay minerals).

5.3.1. Glazed white stone ware

Glazed white stone ware was first developed in the early 1980s by SACMI’s body No. 17, whose formulation clearly represents a rupture from previous schemes: limited use of conventional clays (25% BC), fluxes (7% sodic feldspar) and fillers (10% quartz sand) but appeal to then uncommon raw materials like low-grade kaolin (8%) and especially “eurite” (50%) that is a sericite-feldspar flux, ensuring fusibility, skeleton and some plasticity (SACMI, 1986). From that moment the doors have been opened for an extensive use of unconventional raw materials that, joined to the flexibility of tilemaking process, offer many degrees of freedom in body formulation. In this framework, basic criteria to design GWS batches are (Fig. 12):

- Fe₂O₃ amount of the body in between 1% and 2%;
- clay:non plastic raw materials ratio around 50%:50%;
- preferred use of clays with low to medium plasticity (LK, KL, BC1);
- chance to utilize unconventional fluxes with some clay component (e.g., RK);
- priority to multipurpose raw materials (e.g., raw granite acting as both flux and filler).

As an example, typical recipes in the Sassuolo (Italy) and Castellón (Spain) districts are reported in Table 3, together with a pyrophyllite-based batch.

5.3.2. Porcelain stone ware

Porcelain stone ware represents the top quality floor tiles with the best technical performances and esthetic appearance; both UPS and GPS can be used in wall coverings and ventilated façades too. The UPS typology was developed starting from recipes inspired to porcelain: not a case if early batches did large use of kaolins and limited amounts of fluxes (i.e. PSW1 in Table 3). However, bodies more suitable for fast firing were formulated during the 1990s and their basic criteria are still valid, though with little adjustments for the GPS typology (e.g., PSW2 and PSW4 in Table 3):

- the Fe₂O₃ amount of the body (0.7% on average) must be lower than 1.5%; within this threshold, GPS bodies exhibit higher iron contents.
- Non plastic raw materials are more abundant than the clay component; the clay:non plastic ratio usually ranges from 40%:60% to 45%:55%; it can be even lower in special products: e.g. 30–35% of plastic component in superwhite bodies (Tenorio Cavalcante et al., 2004).
- Clays with medium to high plasticity (BC1 and BC2) are preferred; low plasticity clays (KL, LC, PC) are utilized together with highly
plastic additives (BC3 or WB); the use of BC2 with some BC3 is recommended for large sized and/or thin tiles.

- Although conventional fluxes predominate, especially in UPS batches, unconventional types with some clay component, like RK, may be used if their iron content is low (e.g. <1%).
- Multipurpose raw materials are well tolerated, particularly if they contribute to lower cost and iron oxide average content of the batch.

Porcelain stoneware bodies may contain additives with different purposes: e.g., pigments and opacifiers for through-body decoration of UGS; plasticizers (from WB to organic and hybrid binders) especially for large size and/or thin tiles; sintering promoters (talc, glass-ceramic frits, carbonates, etc.) to fasten densification kinetics.

Along with typical UGS and GPS recipes, Table 3 reports an example of pyrophyllite-based body. In contrast, batches distinguished essentially by the recourse to special fluxes and additives, like anorthite-based, superwhite or translucent UPS, are not considered here.

6. Worked examples

The classification here proposed will be applied to some representative examples of clay raw materials for the ceramic industry, in particular: Miocene clays from the Donbass basin, Ukraine; sedimentary kaolins from Mississippi, Tennessee and Texas, USA; Late Paleozoic clays from Argentina; Cretaceous clays from the Oliete-Teruel basin, Spain; Mesozoic to Tertiary clays from Tunisia.

Ukrainian clays are reknown in ceramic tile production for their plasticity and technological properties (Bal and Fiederling-Kapteinat, 2007; Fiederling-Kapteinat, 2005) to the point they are frequently taken into account as representative of ceramic clays coming from different mines in the Donbass district. As their iron oxide is at most 1.15%, they pertain to light-firing clays and plot into the field of ball clays according to their particle size distribution and kaolinite content (Fig. 13). Depending on their MBI, they are classifiable as medium (BC1) or to high (BC2) to very high plasticity (BC3) implying that not all the Ukrainian ball clays exhibit high plasticity (LK and BC1 terms should be blended with more plastic terms). This classification is in full agreement with the industrial practice, as Ukrainian clays are addressed to porcelain stoneware production (normally 10–30% of the batch) and secondarily to white-firing bodies for porous tiles, particularly when large slabs have to be manufactured or if it is necessary to improve plasticity of other clay components.

Sedimentary kaolins from southeastern USA are here represented by data taken from Wilson (1998). Overall, they present iron oxide content within light-firing clays; their particle size and kaolinite amount spread from RK to HK with most samples in the field where LK and BC overlap (Fig. 13). Samples with the lowest plasticity and the highest kaolinite percentage are classified as RK-LK and HK, respectively; the MBI values of the other samples indicate ball clays with medium plasticity (BC1) plus two high plasticity samples (BC2) and one smectite-bearing sample of very high plasticity (BC3). Both kaolins and ball clays can be widely utilized in tilemaking (Bougher, 1995; Lombardo, 1996) the former in lower amount (especially in WMP and GWS batches) while the latter as the main clay component of light-firing formulations, particularly for porcelain stoneware.

Late Paleozoic clays from Tandilia, Argentina, are distinguished by rather high amounts of pyrophyllite associated with kaolinite and illite (Dristas and Frisicale, 2003). Half of samples characterized by Galos (1979) have enough pyrophyllite (20–33%) to be described as PC and a sufficiently low iron oxide (<2%) to be used in light-firing bodies. Another clay with 15% pyrophyllite is likely classifiable as LK, due to the low plasticity of these raw materials, that however depends on the milling degree (Alló et al., 1997). The remaining sample is a pyrophyllite-bearing illitic red clay (RC2). This picture is in agreement with current industrial use: PC (and LK) are components of GWS, GPS and UPS bodies (for instance GWS3 and PSW5 in Table 3); the RC2 clay can be used in GRS batches.

The case-study of the Oliete-Teruel basin in Spain – taking as example the clays characterized by García-Tomás et al. (1996) – offers a wide range of composition and particle size distribution. Iron oxide widely fluctuates from 1% to 9%, with half of samples below 3%, thus classifiable as LFC. According to their relatively low amount of kaolinite and fraction <2 μm, these clays are in many classes classified as KL or LK; two samples plotting in the BC field can be actually defined medium plasticity ball clays on the basis of their Atterberg plastic index (Fig. 13). Overall, these LFC find application in bodies where they play simultaneously the role of filler and plastic component: e.g., GWS1 and PSW4 batches (Table 3). However, their use must be balanced with high plasticity clays like BC2 or BC3 (Sánchez et al., 1997). The iron-rich clays are rather coarse-grained, with half of samples with a

Fig. 13. Examples of classification of light-firing clays: clays from the Donbass basin, Ukraine (circles); sedimentary kaolins from Mississippi, Tennessee and Texas, USA (triangles); clays from the Oliete-Teruel basin, Spain (squares).

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sandy fraction over 25% (thus classified as red loams). The remaining clays are predominantly kaolinitic and so attributable to the RC1 type (Fig. 14). These DFC are currently used (Meseguer et al., 2011b) in both porous and vitrified bodies up to 20% (RL) and up to 30% (RC1).

A wide set of ceramic clays from Tunisia were recently investigated encompassing Triassic (Medhioub et al., 2010), Jurassic (Hajaji et al., 2010), Cretaceous (Felhi et al., 2008; Hachani et al., 2012; Jeridi et al., 2008) and Tertiary units (Felhi et al., 2008; Jeridi et al., 2008). Common features are their iron amount over 3% (DFC) and their particle size distribution mostly ranging from silty clays to clayey silts. The main distinctive parameters are the amount of carbonates, that discriminates MC and RC, and the clay mineralogy, defining RC2 and RC3 types (Fig. 14). These raw materials appear to be well suited for porous tiles (Azzouz et al., 2011) whose bodies make use of at the same time of MC and RC (that are present in all the geological units). Strategies of batch formulation like RMP3 and RBR2 can be envisaged, entailing the addition of some filler to compensate the rather fine-grained distribution.

7. Conclusions

Ceramic tile manufacturing is a dynamic industrial sector where market trends and technological innovation have created a complex picture of products and processes. This technological evolution has directly entailed raw materials: a really wide spectrum of clays – with an outstanding range of chemical and mineralogical composition, particle size distribution and ceramic behaviour – is currently utilized in tile making. The classical terminology for ceramic tiles and related reference schemes for raw materials are no longer useful to describe and predict the role of clays in tile manufacturing and must be upgraded.

A new and industry-oriented classification has been proposed on the basis of simple chemical, mineralogical, granulometric and rheological parameters of clay materials. It allows a more efficacious and complete evaluation of clay resources (including valuable types not always considered among industrial minerals) along with a realistic assessment of technological potential of clays, readily transferable to the ceramic industry. Although not entailed by this classification, there are chemical features that may affect the suitability of clays for ceramic applications – e.g. F, Cl, S, and further elements mobilized during firing (Dominguez et al., 2012; González et al., 2006) – and must be considered.

The criteria to properly design the batches for wall and floor tiles have been revised, trying to highlight the key properties for each category of ceramic bodies. Besides representative of the industrial practice, the examples of body formulation given with the present guidelines are not exhaustive, as the extreme flexibility of current technology leaves room for further combination of raw materials (fulfilling anyway the key properties of each tile typology).

At all events, both clay classification and body formulation criteria here proposed cannot substitute a thoroughful technological characterization of ceramic raw materials, that should be performed simulating as faithfully as possible the industrial tilemaking cycles (the closer to industrial processing, the more reliable the technological results).

References


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