How to evaluate a raw material for a tile body composition

Gian Paolo Bertolotti

The continuous improvement of tile machinery technology and the increasing of firing cycle speed require always more attention to evaluate in the correct way the raw materials used in body compositions.

Today in many cases producers dedicate more attention to the quality of the machinery and less to the body composition used in production. A beautiful and updated tile plant produces very good tiles only if we take care to the raw materials we use.

From a technical point of view it's important to underline that the first and the main feature for a good body composition is the constancy of the characteristics of raw materials used in production. For this first it's important to select good and serious suppliers but also have the possibility to control directly raw materials is necessary to foresee possible changing before entering in production cycle.

A tile body composition is a mixture of various inorganic substances originating from minerals present in raw materials.

According to commercial classification, we can distinguish between white and red-burning bodies for making wall and floor tiles.

In both cases, the main raw materials used can be divided in the following categories :

a) Plastic raw materials:

Clays , Kaolins

they help ceramic products shaping and give enough cohesion of the body during production.

b) Flux raw materials:

Feldspars, Feldspathic sands, Feldspathoids

they permit glass phase formation and accelerate chemical and physical transformations during firing process. At lower temperatures they act as inert structural materials.

c) Inert raw materials:

Quartz, Silica sands

they help to reduce body plasticity and help to control shrinkage of the products, during firing together with clays, give structure to the ceramic body.

d) Other raw materials

Calcite, Dolomite, Talc

they work as corrective components to reach body specific characteristics.

Kaolinitic plastic clays (Ball clays)

These are fine-grained sedimentary plastic clays in which the clay mineral kaolinite is predominant.

The name "Ball Clay" dates back to the early methods of mining, when clay was dug using specialised hand tools, which extracted the clay in rough cube shapes of about 25 cm each side. As the corners were knocked through handling and storage, the clay cubes became rounded and "ball" shaped.

These clays are usually dark grey until black in the unfired state because of organic impurities, but burn white or light coloured. They have a large proportion of kaolinite but also contain a little illite content and a variety of impurities.

Ball clays are sedimentary clays, originated by erosion of pre-existing kaolinized rocks. They derived from transportation and deposition of these sediments, mixed with other clay minerals, sands, gravels and organic material, in lake or delta basins.

In typical ball clays, there are usually three dominant minerals: from 35-50% kaolinite, 25-35% illite/mica, and 15-35% quartz.

In addition, there are other accessory minerals and some carbonaceous material (derived from previous vegetation). The wide variation in mineral composition, and in the size of the clay particles shows different characteristics for each individual ball clay deposit. The particle size distribution is generally fine, so interesting plastic behaviour can be expected. Ball clays are used in whiteware production to make the body more plastic and workable.

Light-burning plastic clays

They consist of white-burning illitic-kaolinitic clays. They are similar to the ball clays but with a lower kaolinite content. The considerable presence of illite or mixed layer (illite–smectite) clay minerals gets

Photo 1 : Ball clay level (India)

Photo 2 : Light-burning plastic clay (Ukraine)

Plastic clays (Illitic- kaolinitic clays)		Medium plasticity clays (Kaolinitic - illitic clays)		Low plasticity clays (Kaolinitic - illitic clays)	
Quantitative chemical analysis		Quantitative chemical analysis		Quantitative chemical analysis	
	%		%		%
SiO_2	59 - 61	SiO_2	65 - 67	SiO_2	72 - 74
Al_2O_3	25 - 27	Al_2O_3	20 - 22	Al_2O_3	16 - 18
Fe_2O_3	1.0 - 1.5	Fe_2O_3	1.0 - 1.5	Fe_2O_3	1.0 - 1.5
TiO_2	0.5 - 1.5	TiO_2	0.5 - 1.5	TiO_2	0.5 - 1.5
CaO	0.0 - 0.2	CaO	0.0 - 0.2	CaO	0.0 - 0.2
MgO	0.3 - 0.5	MgO	0.2 - 0.4	MgO	0,3 - 0.5
Na_2O	0.1 - 0.5	Na_2O	0.1 - 0.5	Na_2O	0.1 - 0.5
K_2O	1.5 - 3.0	K_2O	1.5 - 3.0	K_2O	1.5 - 3.0
SO_3	< 0.1	SO_3	< 0.1	SO_3	< 0.1
C	< 0.2	C	< 0.1	C	< 0.2
L.o.I.	8.0 - 9.0	L.o.I.	6.0 - 7.0	L.o.I.	4.0 - 5.0
Qualitative mineralogical analysis		Qualitative mineralogical analysis		Qualitative mineralogical analysis	
Kaolinite - Illite - Quartz - Feldspar		Kaolinite - Quartz - Illite - Feldspar		Kaolinite - Quartz - Illite - Feldspar	

Photo 3 : light-burning medium-low plasticity clay (Germany)

worse clay characteristics in aqueous suspension (rheology) but at the same time it improve their plasticity and melting properties.

In these clays, there are usually the following mineral composition: 30-50 % kaolinite, 25-40 % illite/mica, and 10-25% quartz. Colour after firing is light when Fe_2O_3 and TiO_2 content is lower than 1.5 %.

Light-burning medium-low plasticity clays

These raw materials are non-carbonaceous, siliceous clays with medium-low plasticity showing good bending strength values after pressing. These clays usually have the following mineral composition : 20-40 % illite/mica, 15-30 % kaolinite, and 35 – 55 % quartz. They burn with light colour when $Fe_2O_3 + TiO_2 < 1,5\text{-}2$ %.

In the table are synthesizes chemical analysis of standard light firing clays uses in porcelain tile production.

Photo 4: Kaolinized rock exploitation (United Kingdom)

Photo 5: Red burning plastic clay (Italy)

Kaolins (China clays)

Kaolin is a purified white plastic clay primarily composed of kaolinite in association with small quantities of other minerals such as feldspar, mica and quartz. It is called China Clay as it was used in China and later elsewhere to produce very white ware. The word kaolin is derived from Kao Ling meaning in Chinese high ridge, presumably where this clay was mined. It is made up of a loose aggregation of randomly oriented stacks of kaolinite flakes. Kaolin deposits are formed through the alteration, or kaolinisation of feldspar-rich rocks such as granite or gneiss by hydrothermal and/or weathering processes. The mineralogical and chemical composition of the kaolin depends on the nature of the parent rock and the type and degree of alteration. This clay is white firing under oxidising conditions.

The chemical and mineralogical composition of kaolin deposits does not always meet users' requirements and therefore requires refining treatments before being commercialized. In both processes, the refining treatments have the purpose of increasing the material's kaolinite content by reducing as far as possible accessory Minerals such as quartz and feldspars and other impurities. Kaolin is the basic raw material to increase the percentage of alumina in the ceramic bodies. It is coarser grained and less plastic than ball clays, anyway it helps to provides strength and plasticity in the shaping of the ceramics products and reduces the amount of pyroplastic deformation in the process of firing. It converts to mullite and glass when fired to temperatures exceeding 1000°C. It is essential to the achievement of high fired whiteness. This is because it normally contains a lower content of colouring elements than other clayey raw materials.

Red-burning plastic clays (clays for stoneware)

They are semi-refractory clays which contain enough flux to fire at comparatively low temperature (about 1100-1150 °C). They are comparatively plastic without showing too much shrinkage after firing. These raw materials show red/brown colour after firing and they are almost entirely carbonate-free. The clayey minerals can be associated to illite-chlorite types. They give plasticity to the body composition with good bending strength values after pressing, after drying and after firing.

Red-burning middle-low plasticity clays with carbonates

Their composition show mineralogical associations of illite-chlorite and sometimes illite-kaolinite (in lower quantity) with also presence of montmorillonite. Carbonates content in the raw material is variable and it can also reach very high values. These clays help to give plasticity to the body. Usually after firing they present a orange-hazel colour due to the presence of iron minerals.

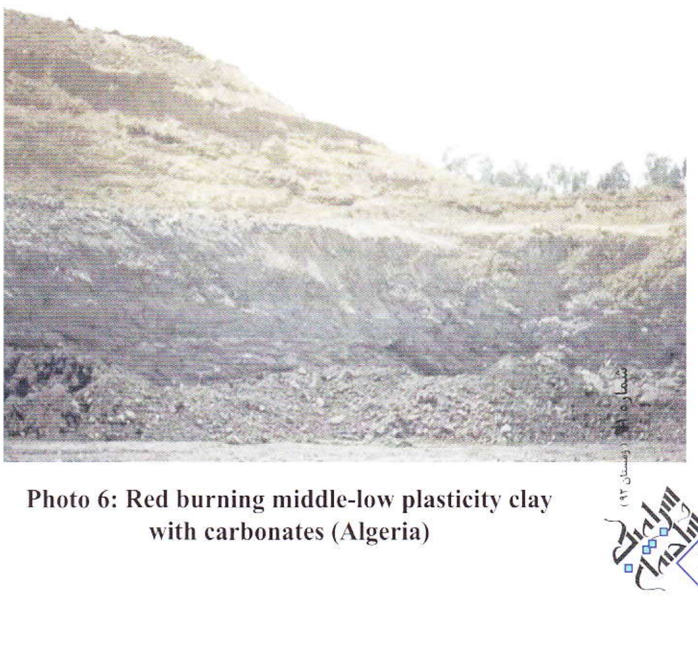

Photo 6: Red burning middle-low plasticity clay with carbonates (Algeria)

Feldspars and feldspar sands

Feldspar minerals are essential components in igneous, metamorphic and sedimentary rocks.

The mineralogical composition of most feldspars can be expressed in terms of the ternary system Orthoclase ($KAlSi_3O_8$), Albite ($NaAlSi_3O_8$) and Anorthite ($CaAl_2Si_2O_8$).

Chemically, the feldspars are silicates of aluminium, containing sodium, potassium, calcium, iron, barium or combinations of these elements.

The minerals of which the composition is comprised between Albite and Anorthite are known as the plagioclase feldspars, while those comprised between Albite and Orthoclase are called the alkali feldspars.

The latter category is of particular interest in terms of industrial use of feldspars. Amongst the numerous rocks in which they are present, feldspars are particularly abundant in igneous rocks like granite, which contains up to 50 or 70% of alkaline feldspar. Granite is however rarely used as feldspar for its iron content (biotite). Rather a whole range of rocks geologically connected to granite are commonly used in ceramic production.

Commercial feldspar is usually exploited from pegmatite or feldspatic sand deposits. Aplite, which is a finegrained igneous rock with the same mineralogical composition as granite is also frequently used for itsfeldspar content. Basically, the two properties which make feldspars very useful for ceramic industry are their alkali and alumina content. On those elements we can distinguish three families: Feldspar sand, Pegmatite and Feldspar. A further distinction can be made between sodium, potassium and mixed feldspars, depending on the type of alkali content.

The feldspars help the formation of the vitreous phase and accelerate the chemical and physical transformations of the particles during the firing process. The feldspars at lower temperatures (as in wall tile products) act as inert structural material structural and facilitate the effusion of the volatile compounds which arise during firing.

In red body formulation acid volcanic rocks as rhyolite and porphyres are used as feldspar source for is high content of potassium feldspar and quartz.

The use of feldspars also helps to reduce and control the thermal expansion coefficient of a ceramic body.

Photo 7: Potassium feldspar deposit (India)

Quartz and silica sand

Quartz and/or silica sand quartz is introduced into the composition as filler in order to facilitate the effusion of the volatile compounds which arise during firing. Quartz is a basic material for adjusting the thermal expansion coefficient, which increase proportionally to the quantity present. Reactivity of free silica against alkaline-earth oxides (CaO e MgO) must be limited and controlled.

Photo 8: quartz (India)

Carbonates

Calcite and/or dolomite are fundamental materials for wall tile bodies, the permit to control shrinkage of porous products. Especially important is their particle size distribution before and after grinding. In fact, very fine particle size distributions favour both decarbonation reactions and, at a later stage, the synthesis reactions with "residues" of original clayey minerals.

Photo 9: dolomite quarry (Italy)

Photo 10 : talc exploitation (India)

Very important are decarbonation kinetics and especially the complete ejection of the gas (CO_2), before the "softening" of the surface glass (glaze). The evolution and completion of synthesis reactions between silica, alkaline-earth oxides and alumina, play a leading role in defining the physical and mechanical features of the ceramic pieces after firing (mechanical strength, thermal expansion coefficient, etc.).

In low water absorption bodies fired at higher temperatures, carbonates added in lower percentage (max 3-4 %) act as energetic fluxes.

Talc

Talc is a hydrated magnesium sheet silicate with the chemical formula $Mg_3Si_4O_{10}(OH)_2$.

At temperatures above 900°C, talc progressively loses its hydroxyl groups and above 1050°C, it recrystallises into different forms of enstatite (anhydrous magnesium silicate). Talc's melting point is at 1500°C.

Talc added in limited percentage in the body composition (< 5%), favors the eutectic reactions of the body acting as energetic flux in low water absorption bodies fired at high temperature.

Other special materials added in body compositions are :

Zirconium silicate or alumina for improve whitness of the body in superwhite porcelain tiles or special frits to give special characteristics to the body composition.

How to control the quality of a raw material and to select it for a body composition

Usually a ceramic raw material is proposed by the supplier with a technical data sheet where are indicated the main characteristics of the material.

Chemical composition is always indicated and in many cases is also indicated mineralogical composition and physical characteristics.

Considering that few tile factories could permit to install in their laboratory the very expensive X-ray equipment for the analysis, some simple laboratory controls must be organized to periodically check raw-material quality.

The first suggestion is to save a 50-100 kg quantity considered as standard to compare with every new arrival of the raw material in the factory.

The simplest method to control is to compare small samples of the raw material with the standard quality firing them in industrial kiln or if available in a muffle kiln.

Physical-ceramic surveys after firing

The following characteristics will be determined after firing:

- water absorption
- shrinkage
- colour
- loss on ignition

The resulting data must be compared with the standard sample of the same material; In case of big differences, the body composition must be changed. The same tests can be run with non-plastic raw materials where, if necessary, some plastic materials can be added (always the same) to prepare the samples. The laboratory manager must always examine the results and has to suggest the changes in the composition if necessary. Obviously the production manager must be informed about the changes to be made and decide when to start a modified composition. Practically the most variable raw materials are clays, so they have to be checked well and more frequently.

Water absorption

Boiling method

The tiles are weighed, immersed into water and boiled for a two hour time; afterwards they remain in the water for further four hours and are successively wiped with a damp cloth and weighed again. The formula to calculate the percentage of water absorption is:

$E[\%]=100*(P_2-P_1)/P_1$

where:

P_2 = final weight of the tile (after absorption),

P_1 = starting weight of the tile (before absorption).

Another way to measure water absorption is according to the method of the sample water impregnation in immersion under vacuum («deprimometer»)

Linear shrinkage The samples are measured only after being fired and the shrinkage is calculated on the difference in dimension in relation to the die cavity. The formula for the calculation of the percentage of linear shrinkage is:

$S[\%]=100*(D_1-D_2)/D_1$

where:

D_1= die cavity dimensions,

D_2= dimensions of the tile after firing

Colour

Although there are special laboratory equipment to evaluate the colour and the ton of the fired material, the simplest way is to compare the colour of the sample with the standard one. A darker colour with the same shrinkage and water absorption means tha t iron and titanium content is higher than the standard.

Loss of ignition

10-20 g of the sample are weighed, properly milled and dryed and then fired in a muffle kiln at 1100 °C with 1 hour at the maximum temperature.

The weight difference before and after firing (P2) divided for the initial weight (P1) and multiplied for 100 give the loss of ignition:

$L.O.I.[\%]=100*(P_1-P_2)/P_1$

If a muffle kiln is not available, it's possible to measure the difference of weight of the same samples before and after firing industrial kiln.

Important controls to do periodically are also the following ones:

Moisture content

Carefully weigh out the amount of powder to be checked to the nearest 0,1g (A). Dry the sample in a drying oven for at least 4 hours until a constant weigh is reached, then weigh it again as quickly as possible, to the nearest 0,1g (B). Calculate the percentage of free moisture, on the dry-mass weight and to the nearest 0,1 percent, as follows:

Free moisture % = [(A - B) / A] * 100

Residue control

A representative weighed sample of each dried raw material is dissolved in water by stirring. Afterwards the obtained slip is screened through a 0,080 micron sieve and the residue is then dried and weighed. The percentage of residue is given by the formula:

Residue % = A/B*100

Where:

A = residual weight [g]

Another important control to do is the evaluation of carbonates present in the raw materials calculated with simple equipment (Calcimeter) that measure the reaction with HCl and measure the emission of CO2.

All these data must be collected in a laboratory database to be ready to verify them when production problems arise.

If a new raw material has to be tested in a production body composition, the best way to operate is to prepare a small laboratory quantity of the standard body composition (with standard of each raw material present in the body) and add an increasing percentage of the new raw material changing step by step the one to substitute in the composition.

When the results are acceptable a semi-industrial test in the plant can be done, prepared in a small mill (example a glaze mill not in production) firstly with few tiles (well identified from the production ones) and step by step increasing the quantity until results are confirmed.

Regarding the study of a new body formulation it's important to start with accurate chemical analyses and after studying a correct balancing of the main oxides of the formulation physical and technological parameters must be studied.

The most important parameters are the following ones:

- Plasticity (M.O.R.)
- Rheology (Viscosity, Thyxotrophy)
- Evaluation of carbonates (Calcimetry)
- Evaluation of soluble salts

- Expansion after pressing (clays and kaolins)
- Apparent density
- M.O.R. (Bending strength green , dried and after firing)
- Water absorption
- Shrikage
- Thermal expansion
- Colour evaluation

Regarding different qualities of body compositions, an extract from the article "On the tiles. Material choice for ceramic bodies" (Martin Stentiford, Industrial Minerals, 2003) is attached:

A tile body is a layer 5 to 20 mm thick that act as structural substrate, except in the case of unglazed tiles where the face also provides the decorative effect. The body brings mechanical strength, dimensional stability and durability.

The body does not generally constitute a marketing feature of the finished piece but is essential to the success of the product. It's important to ensure that while it is fit for its purpose production costs remain controlled and competitive. Such considerations figure strongly in the choice of the raw materials for body preparation.

Edilcuoghi Design from Kale Tile company

Bicottura – porous, twice-fired tiles

Bicottura tiles, while becoming less common in Europe due to the cost of the double firing process, are still widely produced. They have low transverse breaking strengths and cannot be used in flooring applications but are used extensively in wall tiling.

The type of body preferred is known as calcareous earthenware, meaning a porous body in which one of the major components is calcium carbonate. This is usually introduced as milled limestone (whiting) but ground chalk, marble and dolomite can also be used when they are economically advantageous and technically acceptable.

A typical composition can be :
- plastic clays 40 %
- kaolins 10 %
- limestone 15 %
- quartz sand 35 %

Formulation control is important as these tiles demand that certain physical parameters are achieved in the final body.

One such parameter is the thermal expansion of the tile which must be matched to that of the glaze so that the glaze is maintained in slight compression at the end of the process. This reduces the tendency for thermal crazing and eliminates other potential defects such as peeling.

Tiles produced from such formulations would normally be biscuit (first) fired at a temperature of 980-1100°C (slightly higher in fast fire kilns), followed by a glost (second) firing at 960-1080°C (slightly lower than the first firing).

Bodies of this type are not recommended for fast, single firing because the high volumes of gas released can create problems in the final surface finish of the decorative glaze. However, they have a number of technical merits which are valued by manufacturers:

- they can be very light firing (with correctly selected materials) which obviates the need for an engobe layer.
- ceramic bodies of high calcium content have a low firing shrinkage which is quite insensitive to relatively large changes in the peak firing temperature. This makes control of the tile size much easier.
- high calcium bodies, particularly in the presence of small quantities of magnesium, have very low moisture expansions. This markedly reduces the tendency for crazing in service, particularly in wet areas such as bathrooms.

Care must be exercised over raw material selection to achieve the required performance. Generally, the preferred plastic clays are kaolinitic and must fire to a clean, light colour while deflocculating easily. Kaolins are relatively coarse-grained and white-firing; the limestones are clean and non-carboniferous; and quartz sand of low impurity content (though not of glass grade).

Often, a raw (unprocessed) kaolin can be used which contains the necessary kaolin and a part of the quartz in a single raw material, thus saving material costs, and it is common practice that part of the sand is substituted by up to 10% of 'pitcher' (crushed, rejected biscuit tile which arises from the process itself).

Edge Design from Keope Tile company

Monoporosa – porous,once-fired tiles

Monoporosa tiles satisfy a large part of overall market demand in the porous wall tile sector. The main reason for this is cost; the single firing process uses less energy and labour and, through the addition of an engobe layer, a wider selection of cheaper raw materials is available. However, the range of decorativeoptions which can be successfully carried by monoporosa tiles is more restricted than for twice-fired tiles and it is difficult to attain the highest quality glaze finish on these products.

In a single, fast firing process, the chemical and physical changes that occur during the conversion of the raw clayware to the finished article are accomplished at the same time.

To ensure that this runs smoothly, the body must be carefully designed in order to reduce likely losses. Of critical importance is the amount of gas evolved during the firing and which must be vented through the engobe and glaze layers before these become impermeable. Failure to achieve this will result in defects in either the body or the glaze in the finished piece which would result in its rejection or downgrading according to the severity of the fault.

Clearly, one approach to this is to reduce the total amount of gas evolved and to choose body components from which gaseous parts are eliminated both rapidly and at temperatures well below the fusion points of the glaze or engobe.

This restricts the use of calcium or magnesium carbonates and clays with a high content of organic matter.

The resultant body must also satisfy the other technical demands of the process:

- it must be readily deflocculated
- provide adequate plasticity and strength for the forming process
- yield a stable, predictable mechanical base after its ceramic transformation
- meet the demands of the relevant standards.

A typical composition that satisfies these criteria could be:

- plastic clays 45 %
- lean clays 15 %
- feldspar 20 %
- quartz sand 20 %

The clay materials in such bodies may be light firing or fire to give a pink to red colour. This increases the options available to a tile manufacturer as deposits of red burning clays are much more common than the lighter burning clays.

TIENDA HEXAGONAL Design from Land Tile company

Kaolinitic clays are generally preferred to illitic ones as the rates of shrinkage and the final levels of porosity are easier to control. Some raw materials can be combined when suitable alternatives are available, most commonly pegmatitic sands which can be considered as a naturally occurring mixture of feldspar and quartz, or siliceous clays, considered as a mixture of plastic clay and quartz sand.

Commonly, 'pitcher' will also be introduced to these bodies at levels up to limestone may be introduced (about 5%) to reduce the moisture expansion of the body. However, sufficient calcite impurity will already be present in some of the red burning clays.

Tiles in this category will normally be fired to temperatures of 1040-1140°C, with a total firing cycle time of less than 50 minutes. As the engobe and glaze have been applied to the tile before firing, the three regions of the tile mature together. This has advantages and disadvantages:

- careful control of the temperature cycle is necessary to ensure that all the volatiles escape before the glaze
and engobe seal over to reduce the incidence of surface defects.
- the boundaries between engobe and glaze are less distinct and better bonding results. The finished tile
shows less tendency to craze or peel in subsequent service.

Monocottura – vitreous,once-fired tiles

Vitreous (or stoneware) monocottura tiles satisfy the bulk of market demand for flooring applications,
although they can be used as wall tiles. The majority of tiles in this class are based upon coloured bodies,
which range from pale to terra cotta reds and dark browns, and most base their body compositions around
locally available red burning clays.

These tiles may be glazed or unglazed but both will normally come from the once-fired route.

Typical body compositions for this type of ware are:

- plastic clays 65%
- feldspar 10%
- quartz 25%

More than one grade of plastic clay is usu-


Iron Corten Design from NeoLith Tile company

ally used and the preferred qualities are kaolinitic clays with illite and/or chlorite and/or montmorillonite. Such clays have the high strength and plasticity required by the fabrication process but also ensure rapid and homogeneous vitrification. Part of the combination of feldspar and quartz can be substituted by feldspathic sands where they are available.

The preparation of the body is by the wet route, so it is important that the composition can be dispersed and deflocculated reliably. Firing is accomplished in a single stage, typically with a peak temperature of 1120 - 1200°C and a cycle time of 40 to 60 minutes.

As these tiles are designed to be of low porosity, it is essential that the presence of carbonates, organic carbon and sulphates is kept to a minimum or serious flaws result.

Porcellanato – vitreous, porcelain, once-fired tiles

This style of production represents the zenith of the modern tile maker's art and technology; with its great aesthetic appeal, high technical specification, range of available sizes (linear dimensions of more than 1 metre) and variety of surface finishes.

However, body compositions are not particularly unusual. They are very similar to those traditionally employed for the manufacture of chemical or electrical porcelain.

A typical example is:

- Plastic clays 35%
- Kaolins 15%
- Feldspar 30%
- Quartz 17%
- Talc 3%

It is usual that more than one grade of plastic clay is used and the preferred qualities would be kaolinitic clays with illite and/or montmorillonite but with low contents of colouring oxides. Such clays have the high strengths and plasticities required by the fabrication process and ensure rapid and homogeneous vitrification.

Part of the combination of feldspar and quartz can also be substituted by feldspathic sands where these are available. Likewise, raw kaolins can be used in part replacement of the kaolin and quartz.

Talc is often added to lower the vitrification temperature and to increase the rate of vitrification. Occasionally, zircon has been substituted for some of the quartz where very white bodies are demanded, however, this is expensive and brings other technical problems.

As with vitreous monocottura tiles, it is essential to ensure the content of carbonates, sulphates and organic carbon is very low, but stringent control of colouring oxides is also required so that the body colour after firing remains as white as possible.

Porcellanato tiles are produced with a very wide range of finishes – glazed and unglazed – which can be polished or unpolished with the 'natural' (white) body or with body randomly flecked throughout with other colours (granito). Firing is achieved in a single stage, typically with a peak temperature of 1140-1230°C and a cycle time of 40 minutes to 2.5 hours.

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