

## NATURAL RAW MATERIALS IN “TRADITIONAL” CERAMIC MANUFACTURING

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### ABSTRACT

New typologies of ceramic tiles represent well all the innovations in body and glaze compositions, preparation of powders, application of new integrated industrial strategies, and consequently rational utilization of all the necessary raw materials available. Italy is a representative example of growing of the ceramic tile industry, being one of the larger producer of wall and floor tiles in the world. The optimal utilization of minerals and raw materials is directly proportional to the level of knowledge about the ceramic materials and the effects of minerals and their impurities on the process and on the properties of the end-products. The same mineral can be used for simple, bulk products, but after small modification it may well be used for high quality products.

**Keywords:** ceramics, clays, feldspars, wollastonite, modification, lithium minerals, natural chromite, mullite, zircon.

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### INTRODUCTION

#### CLAYS

##### *General aspects*

The bodies for industrial production of “traditional” ceramic materials (tiles, bathroom fixtures, tableware) are composed of various typologies of raw materials in amounts characteristic of the product desired. The composition of the body and the conditions of treatment determine the transformations that involve the raw material and mainly define the final characteristics and field of employment of the finished product.

With regard to “*traditional*” ceramics, the plasticity, i.e. the possibility of lending workability, shape and sufficient consistency to the ceramic item through the various stages of manipulation is obtained by using “*clays*”. “Clays” is the name generally given to all or more or less compacted sedimentary rocks deriving from alterations of primary rocks, mainly containing “*clayey minerals*” of micron dimension and characterized by high plasticity.

The clays are natural systems and thus extremely heterogeneous; they can be classified on the basis of the prevalent clayey minerals and hence we may distinguish

kaolinitic, montmorillonitic, illitic, chloritic, chloritic-illitic clays, etc.

As well as the clayey minerals described, the clays contain, or may contain:

- accessory minerals retraceable to the primary rock from which they were generated by alteration;
- minerals formed as product of reaction following alteration;
- contact accessory minerals (or components) during the formation of the deposit.

Typical common components accessory to the clayey minerals present in clays are feldspars, quartz, iron oxides and hydroxides, titanium oxide, calcite, dolomite and organic substance. The “*quality*” for ceramic applications of a clay is not an absolute parameter but depends on the type of employment and is evaluated, apart from the factors of economic, logistic and management type, mainly on the basis of a series of considerations as follows:

- Plasticity. This stems from the size of the particles and the typology of clayey minerals present. In general, an increased plasticity is due to the presence of clayey minerals in which the layers are weakly bound (minerals

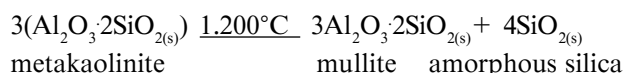
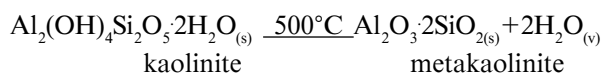
of montmorillonite and/or illite nature), to the reduced size of the particles, to the low order crystal structure and to the presence of organic substance (e.g. ball clays). The plastic clays increase the mechanical resistance in the green state and hence reduce the defects connected with all those phases involving mechanical stresses on unfired tiles (transport, glazing, brushing, etc.).

- Content of iron and titanium oxides with chromophore action. After firing of the item, the presence of iron and titanium oxides or hydroxides determines the appearance of colouring whose intensity depends on the content of the two chromophore oxides and their transformation in the body and the firing environment. The iron and titanium oxide content must be reduced to a minimum in the case of ceramic products to be coloured in the mass (e.g. porcelainized stoneware) or not glazed and of high quality (porcelain).

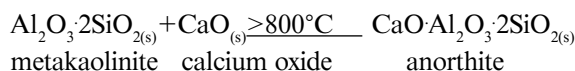
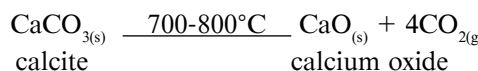
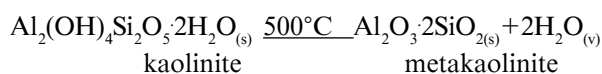
- Content of organic substances. The presence of organic substances may increase the plasticity of the system but, especially in rapid cycles and in bodies containing iron oxide and strongly compacted in the raw state, it creates problems connected with their oxidation ("black core"). The same problems occur in presence of sulphides.

- Deflocculability. Since wet grinding is the most widespread process for treating raw materials, very plastic clays are also generally hard to deflocculate. Generally speaking, problems of deflocculation can be ascribed to the presence of clayey minerals in which the layers are weakly bound (minerals of montmorillonite and/or interlaminated illite/montmorillonite nature), to the reduced particle size, to low-order crystal structures and to the presence of ions with high charge density such as contraions of the negative charge of the layer.

- Capacity to develop mullite. Not only do the clayey minerals perform a plastifying function, they are also important for consolidation of the ceramic item during firing since, after heat treatment, they are able to react leading to the formation of new crystalline and amorphous phases. Mullite is a crystalline phase that develops after the sequence of thermal transformations of kaolinite. The presence of mullite and the resulting formation of amorphous silica by heating above 1100°C favours obtainment of ceramic products with high tenacity and having excellent surface mechanical properties (porcelainized stoneware).



- Content of accessory minerals. The presence of certain minerals, in particular calcite or dolomite, modifies the reactivity of the clayey minerals and, especially, leads to the formation of aluminosilicates of calcium (in particular anorthitic plagioclase) that inhibit the formation of mullite but enable consolidation at low temperatures with formation of porous products.



- Metallic impurities. These generally stem from the machines employed in the working stages. They are generally iron alloys or steels and must be eliminated before using the raw material by magnetic deferrization systems, in order to avoid the occurrence of blemishes on the surface of the finished products.

### Clays in formulation of ceramic bodies

Clay based minerals are the main constituent of ceramic bodies; their amount generally ranges from 40 to 60 wt %. They confer plasticity and workability in the green state and furnish the main oxides involved, with fluxes and sintering aids, in the consolidation mechanism of the body during firing. Technical and economical potential of clays and clay minerals, including those utilized today only in small extent or not at all, could be enhanced by tailoring of mixes or assessing their properties.

The clays used should have properties advantageous for modern continuous wet-processing (easy deflocculability in water), workability (plasticity, body formation, drying behaviour, dry bending strength, sintering and firing behaviour) and quality (colour and

Table 1. Chemical and physical characteristics of the raw materials suitable for the productions of unglazed porcelainized stoneware tiles (from SACMI).

Oxide	A	B	C	D	E
SiO <sub>2</sub>	48/50	62/66	69/71	97/98	51/52
Al <sub>2</sub> O <sub>3</sub>	35/38	23/27	18/20	0.5/1	8/9
TiO <sub>2</sub>	0.1/0.3	0.2/0.5	0.2/0.4	-	0.2/0.4
Fe <sub>2</sub> O <sub>3</sub>	0.2/0.4	0.3/0.5	0.2/0.4	0.2/0.4	0.5/0.7
CaO	0.2/0.4	0.5/0.8	0.1/0.3	0.1/0.2	0.2/0.4
MgO	0.2/0.3	0.3/0.6	0.1/0.5	0.1/0.2	29/31
Na <sub>2</sub> O	0.3/0.6	0.5/0.8	6/7	0.1/0.3	0.1/0.2
K <sub>2</sub> O	0.3/0.7	1.3/1.6	1/1.5	0.1/0.2	0.1/0.3
L.I.	12/13	6/7	0.3/0.5	0.1/0.2	7/8
Organic matter	0.1/0.2	0.2/0.3	-	-	-
Breaking load (Kg/cm <sup>2</sup> )					
Green state	6/10	12/20			
After drying	12/18	20/30			
Firing to 1100°C					
Porosity (%)	10/12	3/6			
Shrinkage (%)	7/8	4/6			
Breaking load (Kg/cm <sup>2</sup> )					
	120/150	250/350			

A) kaolinitic clay; B) plastic clay; C) fluxes; D) quartz; E) talc

transparency of the body). With regards to raw materials there are two essential trends to tackle the problems: use of general raw clays, or use of clays specifically adapted to special technology products. For instance, the single firing technology entails the use of raw materials which have extremely high dry-bending strength. In this context, and taking also into account the use of lower quality raw materials, a more careful characterization of the admixture and the necessity of adapting the composition of the bodies to improve the final products.

As general consideration, kaolinitic clays can improve the formation of mullite and chloritic clays can improve a consolidation mechanism based on formation of crystalline phases containing alkali-earth elements. The presence of mixed layer-impurities with smectitic component may modify the technological properties in a considerable extent, because if a definite effect on the essential behaviour of the clay-water system,

the sintering process and the ceramic body. Kaolinitic clays, in general, by widening the sintering temperature range reduce swelling and deformation of tiles during firing. Germany, England, France and recently East Europe Countries (Bulgaria and Ukraine) are the main suppliers of low-iron clayish raw materials for white bodies.

#### Considerations

Clay based minerals are the main constituent of porcelainized stoneware bodies; their amount generally ranges from 40 to 60 wt %. They confer plasticity and workability in the green state and furnish the main oxides involved, with fluxes and sintering aids, in the consolidation mechanism of the body during firing. With regards to raw materials there are two essential trends to tackle the problems: use of general raw clays, or use of clays specifically adapted to special technology products. For instance, the single firing technology

entails the use of raw materials which have extremely high dry-bending strength. In this context, and taking also into account the use of lower quality raw materials, a more careful characterization of the admixture and the necessity of adapting the composition of the bodies to improve the final products. The clays used are prevalently kaolinitic and should have properties advantageous for modern continuous wet-processing: easy deflocculability, plasticity, high dry bending strength and in particular low titanium and iron oxides content that is fundamental in developing colors.

## **FELDSPARS**

The feldspars are the most common mineral group in the crust of the earth. Feldspars are tectosilicates. They have the same basic structure as quartz, except that one in every four Si is replaced by Al. Therefore, instead of  $\text{Si}_4\text{O}_8$ , feldspars contain  $\text{AlSi}_3\text{O}_8$ . As Al has a  $3^+$  charge, whereas Si has a  $4^+$  charge, the resulting charge difference is made up by K or Na for the alkali feldspars, and by Na and Ca for plagioclase feldspars. There is an additional complication, however, in that Ca has a  $2^+$  charge. For Ca feldspars, therefore, there needs to be a replacement of two in every four Si are replaced by Al. The end members of the feldspar series are Anorthite -  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , Albite -  $\text{NaAlSi}_3\text{O}_8$  and Sanidine/Microcline/Orthoclase -  $\text{KAlSi}_3\text{O}_8$ .

Generally the materials used for the ceramic bodies are clayish materials and hard ones with fluxing properties.

The clayish materials include illitic-kaolinitic clayish minerals with more or less remarkable plastic characteristics depending on the mineralogical nature and on the material particle-size distribution.

The hard materials include feldspars feldspathoids, eurites, pegmatites and eventually quartz.

The main characteristic of all these components is the low amount of colouring oxides such as  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  which allows to avoid any possible colouring change of the bodies. Obviously the quantities of the different clayish materials, the fluxes and eventually quartz depend on the mineralogical nature of the clays, on their particle-size distribution and finally on their reactivity to the fluxes. In general a plastic clay because of its green plastic characteristics is responsible for the workability at the presses and the breaking load after

drying. A china clay is complementary to the previous one as to the green characteristics while it is essential from a chemical point of view as «bearer» of alumina. Feldspars, and eventually talc in small quantities, are to be considered as fluxing agents. Quartz helps to balance the viscosity of the glass phases and is the basic matrix of the glass phase in the finished product.

## **OTHER MINERALS**

### ***Wollastonite***

Wollastonite is a natural calcium silicate. Of predominantly fibrous nature, it became commercially interesting in the United States in 1952 when a large and very pure deposit was discovered in the environs of Willsboro (NY).

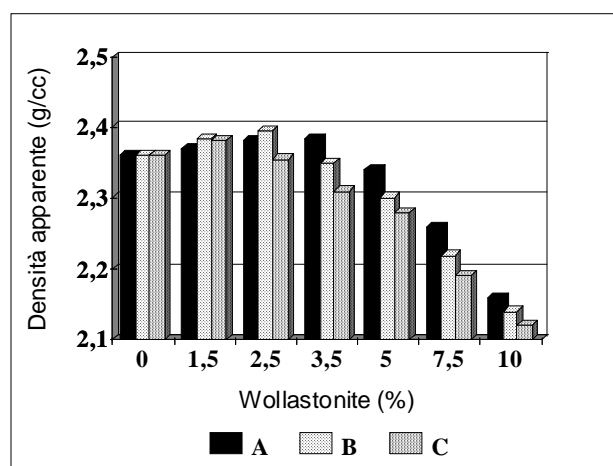
The mineral has aroused considerable interest, especially in the late 1980s, owing to the numerous industrial uses to which it lends itself. Twenty years ago, world production of wollastonite was estimated at around 40,000 tons per year; but expansion of the market for this product has been so rapid that, today, US production alone is estimated at 150,000 tons per year. Currently, the leading world producers of wollastonite are the United States, the People's Republic of China, India and the countries of Northern Europe.

The considerable interest in wollastonite stems from its many applications, especially in the fields of ceramics, plastic materials and metallurgy.

The applications in ceramics are not yet completely defined. Wollastonite has a high fluxing action that enables lowering of what is generally defined as "the point of maturation of ceramic bodies". As well as this - and unlike calcium carbonate - in the industrial production of porous ceramic bodies, wollastonite does not develop gases during firing. This enables it to be used successfully especially in the production of porous single-fired products at low temperatures, where the glaze melts at a temperature below that at which carbonates decompose.

Ceramic bodies obtained by using wollastonite tend to vitrify between 1200 and 1250°C, and are generally characterized by low dielectric loss and good mechanical resistance (application in the sector of electrical insulators).

In semivitrified ceramic bodies, the presence of 1%-3% wollastonite instead of quartz and fluxes enables a reduction in shrinking and re-expansion caused by



the humidity, and an increase in the product's mechanical resistance. By substituting 2%-5% feldspar and quartz with wollastonite, a reduction in the sintering contraction and a lower vitrification temperature can be achieved.

For a variety of reasons, wollastonite is becoming more and more important for ceramic applications in the production of tiles. In floor and wall tiles - the sector in which it is most used, especially in the United States - wollastonite makes for a certain uniformity of size, low shrinking, good resistance, low deformation, low post-firing re-expansion in presence of humidity, and a decrease in the development of gas during the rapid firing cycle. It has thus been the focus of increasing attention in the field of bodies for rapid firing (<30 minutes). Other advantages can be sought in obtaining bodies with a certain permeability, which makes for earlier degassing. Wollastonite reduces the tendency to blackening in paving bodies with a high clay content, causes the formation of "black core", and is also able to reduce the tendency of the material to dirty and to chip.

The criteria for assessing the quality of wollastonite for ceramic uses are generally based on determination of the tenor of iron and titanium minerals (that may give unwanted coloring to glaze and body) on the calcite content (that must be as low as possible, if the product is to be used in glazes and bodies destined for quick firing cycles), and on the presence of occasional impurities, such as metal fragments, that may lead to extremely unpleasant defects on the surface of the final product. Wollastonite is a raw material of considerable ceramic interest that may find several applications, in the preparation both of frits and of ceramic glazes, but

also as an enhancer of sintering in the formulation of bodies for producing porcelain stoneware.

Wollastonite, in suitable amounts and without altering the firing conditions, effectively promotes sintering, enabling the apparent density of the pieces to be increased and their stainability to be reduced. For this application, experimental results have shown how a reduction in the granulometry of the wollastonite particles (which increases its reactivity towards dehydroxylation products) enables a reduction in the quantity.

#### **Lithium minerals**

Traditional lithium minerals applications are the production of low thermal expansion glass-ceramics, low thermal expansion fully vitrified ceramics, frits and glazes. Lithium reduces the glaze viscosity and the melting temperature. In low thermal expansion ceramics and glass-ceramics, the addition of lithium and promotion of  $\beta$ -spodumene is the basis for production of glassware with extreme heat shock resistance. In recent years, extensive research was undertaken in Italy on glass-ceramic glazes for wall and floor tiles. Traditionally, lithium carbonate has been the lithium source in frits and glazes. However, through 1994, there was a continuing trend toward replacing lithium carbonate with lithium minerals, for cost-saving reasons only. Delivered prices of lithium minerals vs lithium carbonate can reduce the cost. Extensive research was undertaken on the possibility to improve properties of ceramics by lithium minerals, although the work acknowledges that individual research on particular bodies and firing conditions may be necessary, the main conclusions are: incorporation of lithium into the body leads to increased activity of the glassy phase during the consolidation process; the increased reactivity results in reductions of both firing times and temperatures; linear contraction of tile during firing is reduced and, as a consequence, losses caused by imperfections in size are decreased; there is improved surface quality of the tile in terms of "spot" resistance and developing of colors.

#### **Natural Chromite**

Chromium oxides are used to provide color to ceramics and are used in conjunction with other compounds to make shades of blue, green, gray and black. Ferrochromium fly ash, and in particular natural

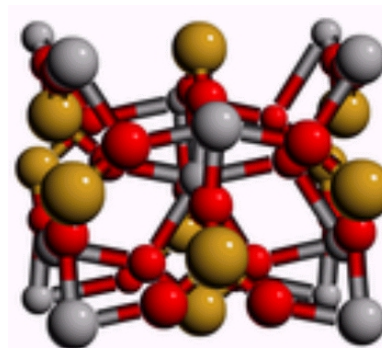
chromite were studied as a source of chromium compounds for coloring unglazed ceramic tiles. Chromite resulted to be a low expensive natural colouring agent to make shades from gray to black as a function of amount and particle size distribution of the pigment, and firing conditions.

#### **Mullite - $3Al_2O_3 \cdot 2SiO_2$**

The name/word “*mullite*” is derived from the Isle of Mull of the Scottish coast, where naturally occurring deposits of mullite have ever been found. Naturally occurring mullite is so rare because it is the result of extremely high temperatures that have come into contact with aluminosilicate minerals of just the right type. Mullite rarely occurs as a mineral in nature. Mullite is the mineralogical name given to the only chemically stable intermediate phase in the  $SiO_2 - Al_2O_3$  system. Mullite is commonly denoted as  $3Al_2O_3 \cdot 2SiO_2$ . However it is actually a solid solution with the equilibrium composition limits of 60–63 mol %  $Al_2O_3$  below 1600° C. Mullite (synonyms: aluminum silicate; CAS Number: 1302-93-8) is the synthetic, fused (or calcined), crystalline aluminum silicate produced in electric arc furnaces from calcined or Bayer process alumina and silica. It has short prismatic crystals. It has low porosity, high resistance to slag attack, good stability in ceramic bonds, excellent volume stability and low shrinkage. It is also available milled and as a spray-dried, sintered, or hollow microsphere product.

#### **Zircon**

The ceramic market accounts for >60% of zircon consumption. The principal and fastest growing use for zircon in ceramic industry is as an opacifier in ceramic glazes. It is used mainly in a wet-milled (micronized) form, with a major property being its high refractive index. It is also used in dry-mill form (325 mesh) for frit production. Low impurity levels, especially iron and titanium oxides, are required. The importance of ceramics application is best exemplified by the explosive growth in demand for zircon for bodies in whitening unglazed porcelainized tiles (consumption of



about 10,000 t/y in Italy). Actually there is no real substitute for opacifier-grade zircon.

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