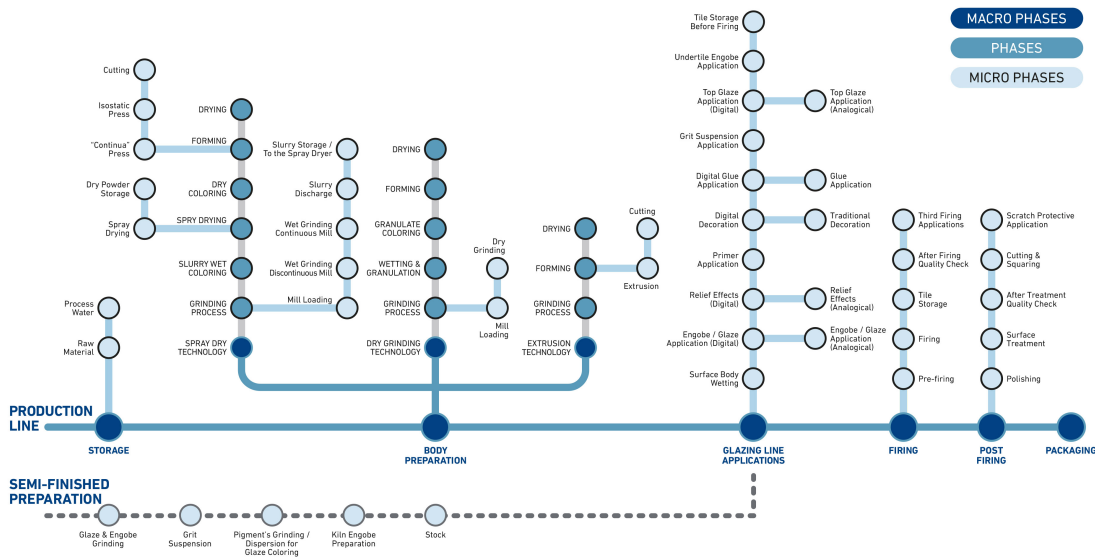




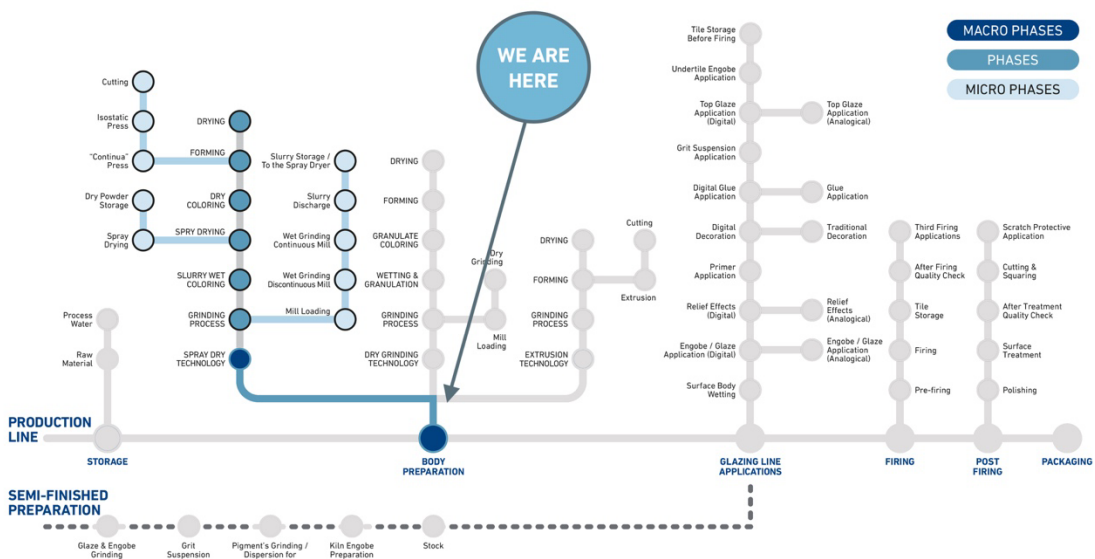
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APPARENTLY INVISIBLE YET CONSTANTLY PRESENT At every stage of the ceramic production process

A journey through problems & solutions



#23 DEFLOCCULATION OF CERAMIC MIXTURES: WHAT ARE THEY & HOW DO THEY WORK?





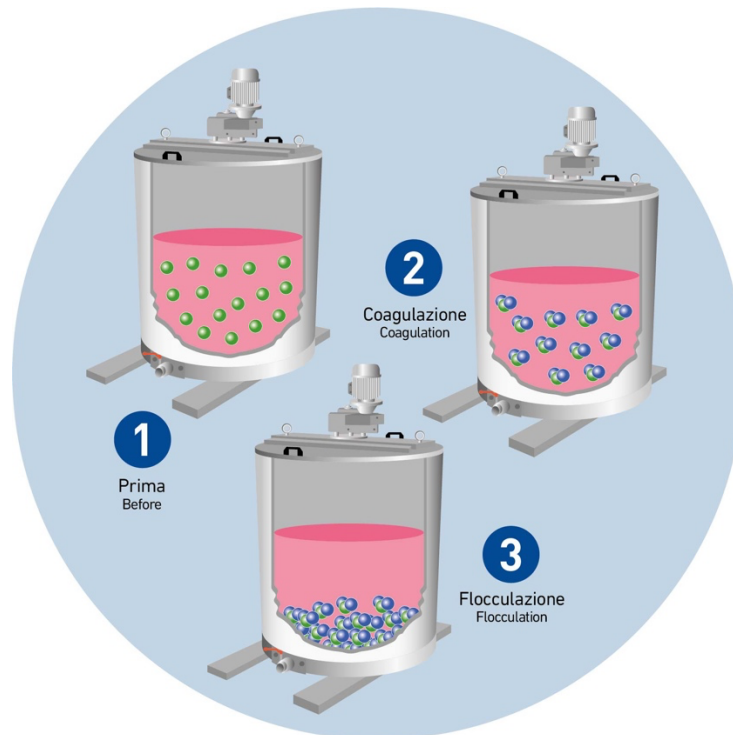
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1. FLOCCULATION: A SHORT DEFINITION

Flocculation phenomena consist of chemical-physical process of a colloidal system within which the solid part tends to separate, leading to flocs in suspension.

In chemistry, it is the stage that follows the coagulation process, during which the particles of the colloid produce small aggregates, so-called flocs, that may precipitate.



2. INTRODUCTION: THE CERAMIC MIXTURE

The preparation of a ceramic mixture involves several steps that, one after the other, turn the raw materials into high performing ceramic surfaces, both technically and aesthetically.

To put it simple, we list here the most significant:

1. GRINDING
2. SIEVING



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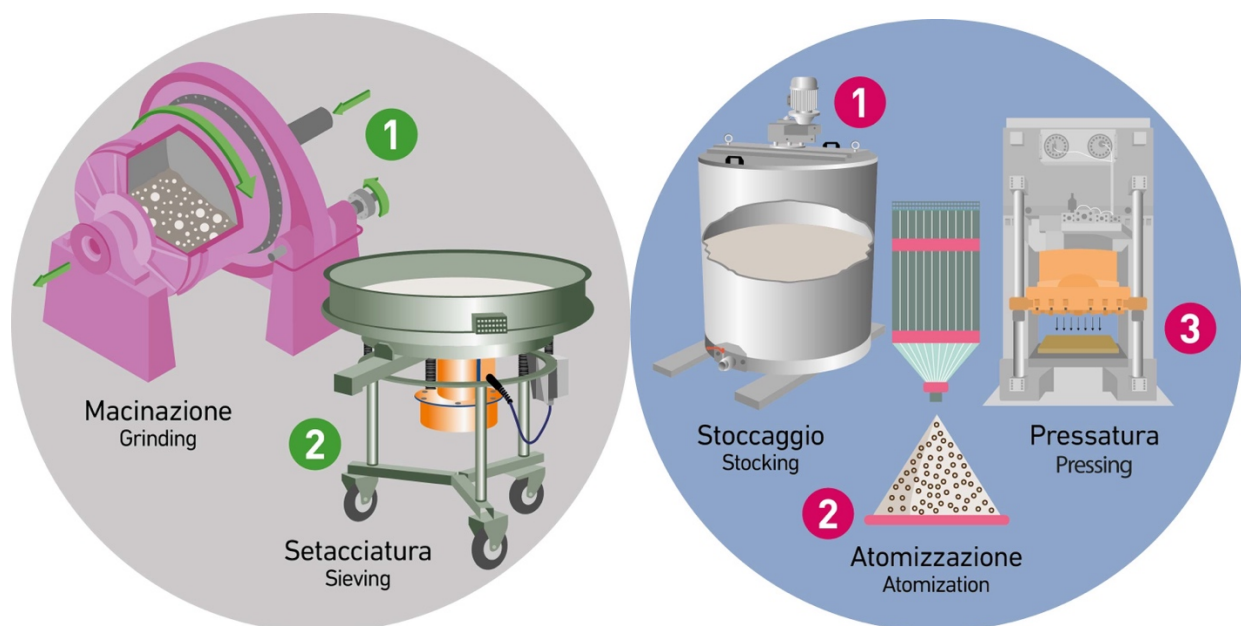
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3. STOCKING
4. ATOMIZATION
5. PRESSING/FORMING

Before talking about flocculation phenomena, let us briefly review these important stages. Ceramic mixtures, before the forming phase (during which the atomized powders are pressed or compacted), is subjected to a wet grinding process that involves the use of grinding waters (recovery and groundwater). At this stage, the inorganic raw materials (sands, clays, feldspars, etc.) together with the water, form the slip also called barbotina.

The grinding process takes usually place by means of Alsing mills and, once the barbotina has been produced, it is sieved and then stocked in tanks where it rests under constant stirring, to avoid possible gelling or sedimentation phenomena.

After stocking – whose duration can range according to producers' need – the slip is nebulized by means of spray dryer to rapidly and violently evaporate the water content thanks to the use of very high temperatures. The evaporation process turns the drops of the slip into tiny hollow spheres that make up the atomized powder, ready to be pressed or formed.



3. FROM A CHEMICAL POINT OF VIEW, WHAT IS A CERAMIC SLIP?

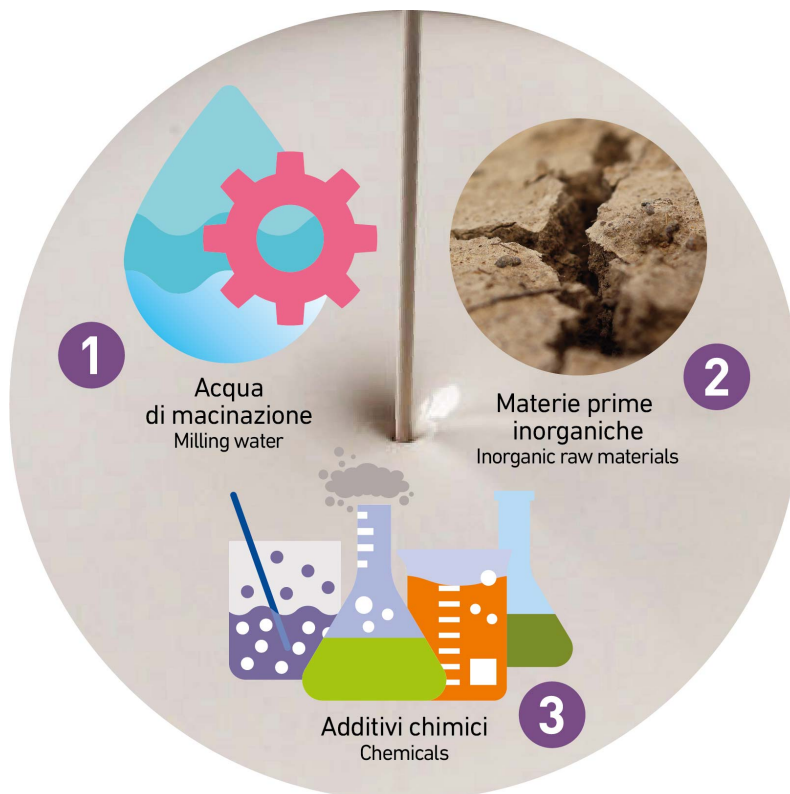
The slip is a **water suspension of clays** (that can be more or less plastic according to the needs) **and other inorganic raw materials** (such as feldspar or sands).

We talk about suspension – and not about solutions – since the ceramic slip a mixture in which the solid part is finely divided and dispersed in a liquid part (the solvent) in order avoid too rapid sedimentation phenomena. The amount of solid part of a suspension is usually smaller than the liquid part.



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4. THE CLAY MICELLES

WHAT ARE THE MAIN FEATURES OF CLAYS WITHIN THE BARBOTTINA?

Clays, for their very nature, generally tends to show an important thixotropic effect that must be managed and removed to let the slip properly flow.

Thixotropy, in simple words, is the property of pseudo-plastic fluids to change their viscosity over time when subjected to a shear stress or a sollicitation, moving for example from a pasty state (we could say almost solid) to a fluid state.

Ceramic slips, because of their structural characteristic, are usually marked by this feature: while they are resting, they seem to be gelatinous but when stressed by an external force – such as for example a simple stirring – can become immediately fluid.

And this is not always good.

Let's now look closer at the reasons why thixotropy must be faced, also high-lighting the basis of flocculation phenomena.

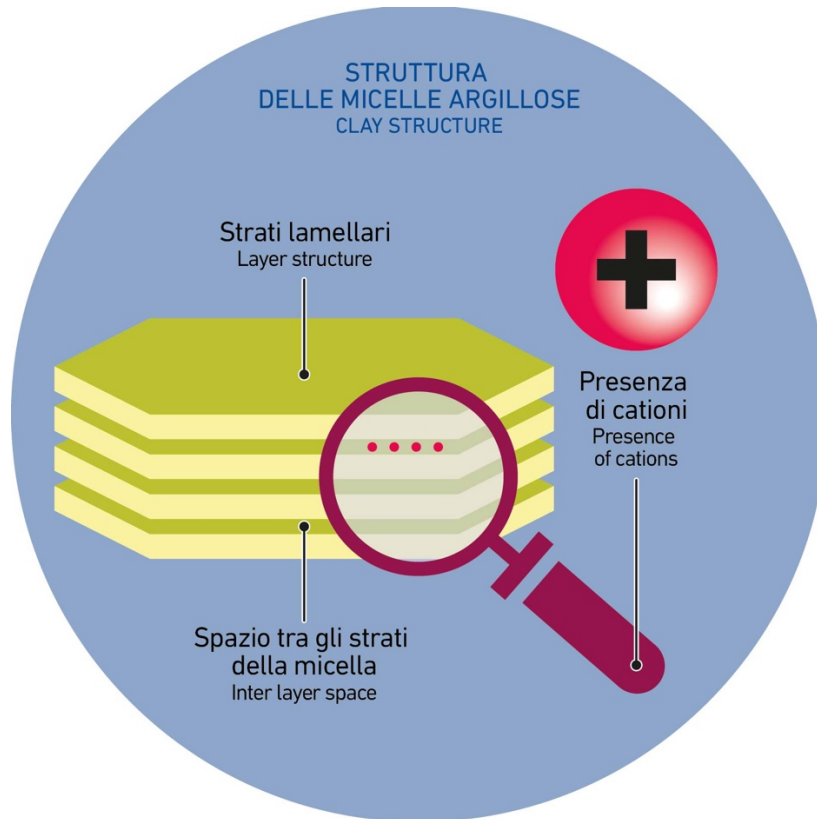
We assume that clays are minerals made up of octahedral and tetrahedral sheets of Al_2O_3 (aluminum oxide) e SiO_2 (silica). The sheets can be arranged in a wide variety of positions according to the type of clays but, in any case, between one sheet and the other there can be cations of a different nature



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(both monovalent and multivalent). Regardless of the kind of cations, once the clays have been dispersed in water, the octahedral and tetrahedral sheets tend to expand due to the water that filters between the gaps (the space between the sheets). This movement may sometimes lead to the release of cations, that are in these gaps, within the suspension.



THE MICELLE'S ELECTRIC CHARGE

Moreover, the sheets – also called clay micelles – are mainly marked by a positive charge on their border and by a negative charge on the two surfaces (the upper and the lower surfaces of the clay sheet).

This morphology – especially in case of low water amounts within the suspension – produces an electrostatic attraction between the positive and negative charges that leads to a structural effect that increases the system's viscosity. In some extreme cases, the system can jellify, becoming a serious problem for the proper development of the production process.

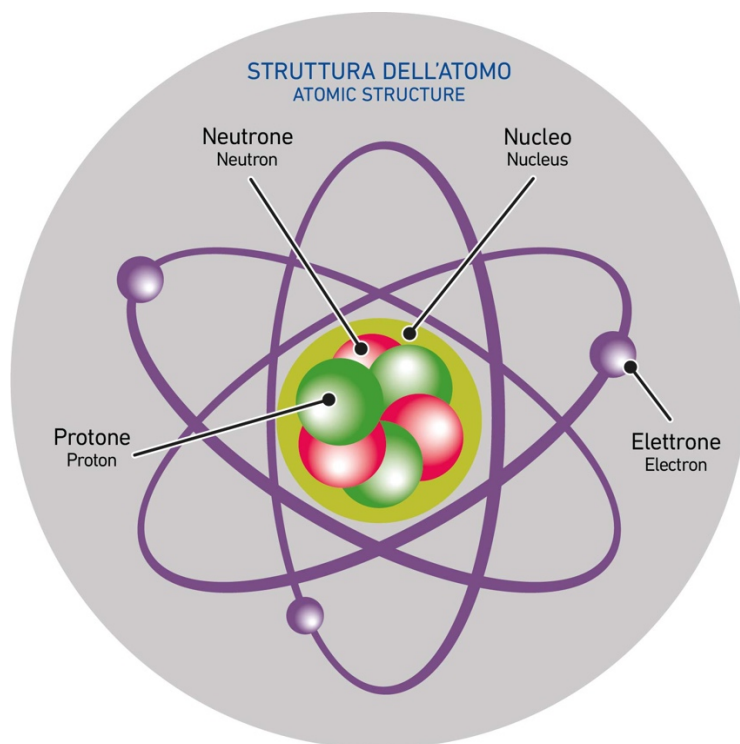
To make the system fluid again – and therefore to generate a deflocculation effect – it is important to give mobility to the clay micelles and to the particles in suspension. To make this happen, there are some important mechanisms to consider, that are the basis of the deflocculation process.



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5. THE MECHANISMS UNDERLYING THE DEFLOCCULATION PROCESS



A) ELECTROSTATIC REPULSION BY CATIONIC EXCHANGE

The multivalent cations – with a double positive charge (such as calcium and magnesium) or with triple positive charge (such as iron or titanium) – are marked by a very high charge, capable of breaking the strong negative charge that is on the micelle's borders. The negative charge is nevertheless important to keep the repulsion force between the micelles, ensuring their flow (think about the repulsive force between two identical magnets). The addition of monovalent cations within the system (such as sodium) allows the replacement of the multivalent positive charges with weaker electric charge (CATION EXCHANGE). This specific cationic exchange decreases the positive electric charge on the micelles without neutralizing the negative ones.

That's the origin of the de-agglomeration effect and of the decreasing of the system's viscosity.

B) STERIC REPULSION

It is produced by using polymeric dispersants made up of inactive molecular chains (that do not produce any interactions with clays and raw materials). However, these dispersants also contain functional group able to interact with them.

The edges of these molecules interact with the slurry's suspended particles increasing their distance. Polymeric dispersants, in other words, bind themselves together with particles (through the functional group) in a specific position that produces the proper distance that is requested to let the particles flow one on the other, avoiding electrostatic interaction that usually arises between the positive and negative charge of the micelle. This phenomenon is responsible for the viscosity reduction, and therefore for the deflocculation effect.



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C) COMPLEXATION

Complexing agents are formed by particular chemical molecules provided with functional groups containing atoms (such as oxygen or nitrogen) that provide the system with a very negative electronic charge.

This charge ideally attracts multivalent instead of monovalent charges.

Once complexing agents have been added to the slurry, they release sodium (monovalent cation), attracting multivalent cations (such as calcium, magnesium, iron or titanium). The final result of this process is the removal of the multivalent charges from the system and the recirculation of monovalent charges: this facilitates the cationic exchange, increasing the distance between the particles, decreasing the viscosity value and therefore reducing the flocculation.

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