

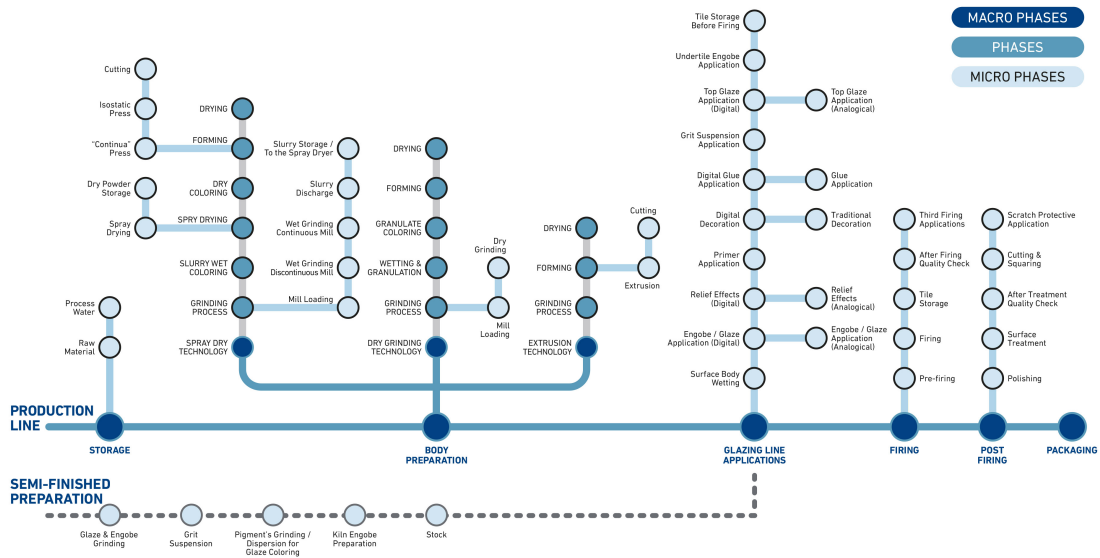


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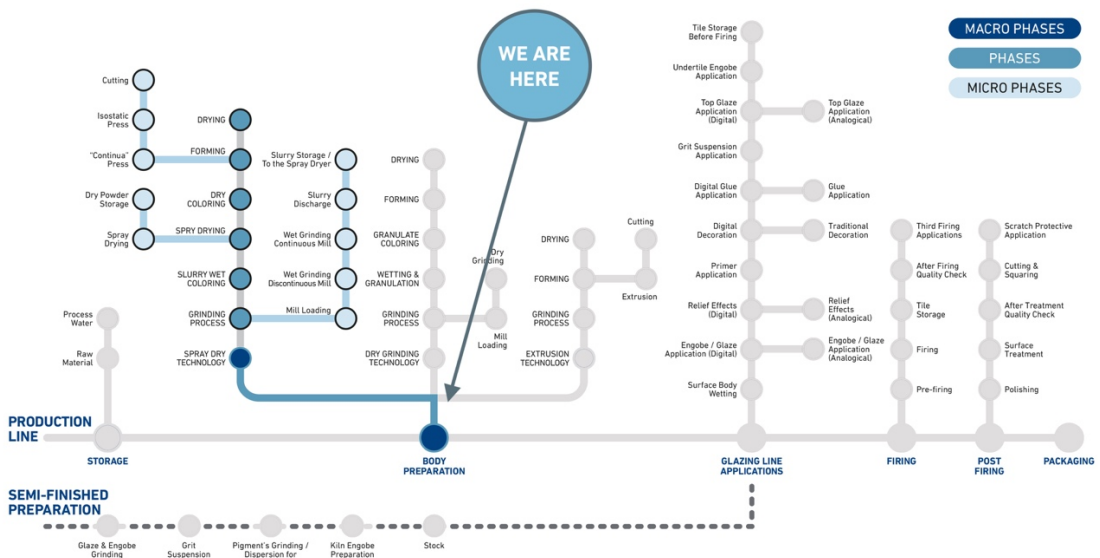
APPARENTLY INVISIBLE YET CONSTANTLY PRESENT

At every stage of the ceramic production process

A journey through problems & solutions



#14 CHEMICALS FOR CERAMIC MIXTURE: AN OVERVIEW





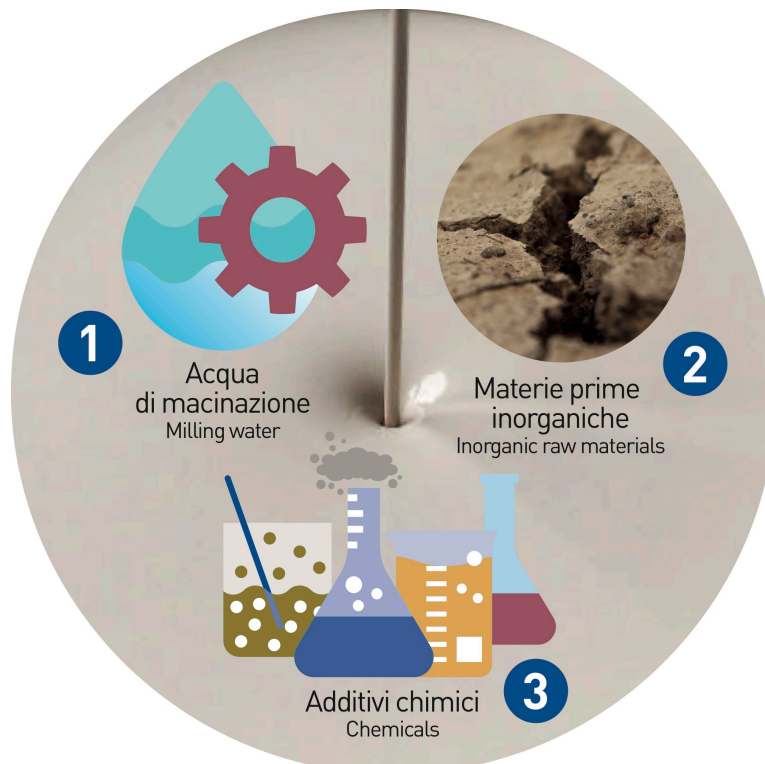
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1. INTRODUCTION

Ceramic mixtures used in tiles production, both for floor and wall, are largely made up of:

- Inorganic raw materials (clays, feldspars, sands, etc)
- Milling water
- Chemicals

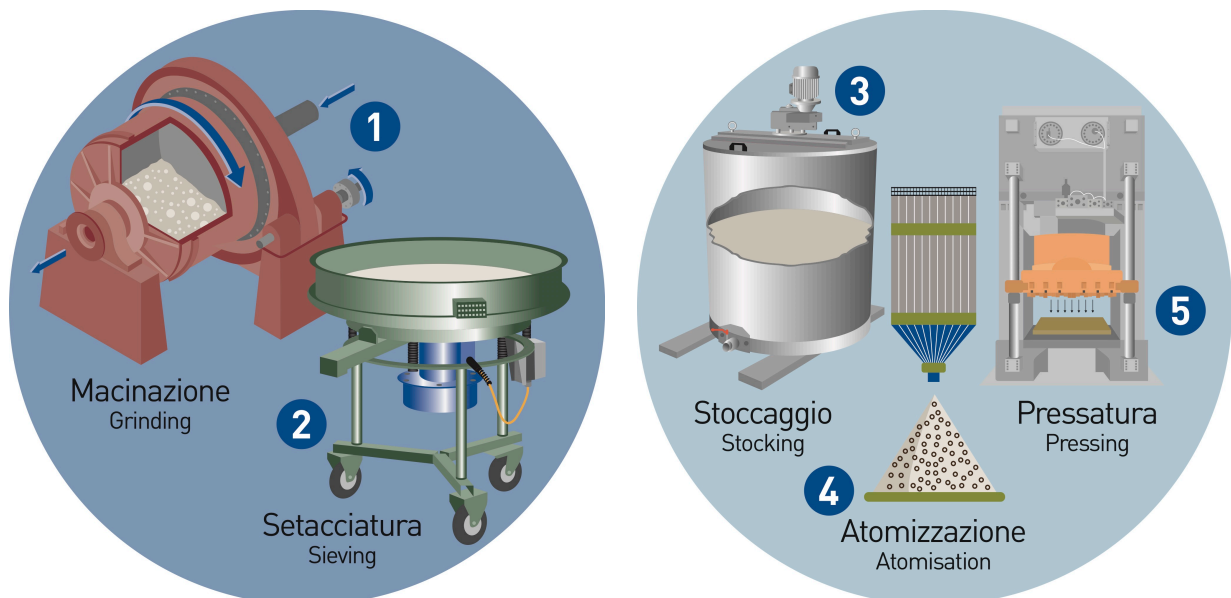




2. FROM THE RAW MATERIAL TO THE RAW TILE

Following here the 5 most important steps that turn the raw materials (and so the ceramic mixture) into a raw tile:

1. GRINDING
2. SIEVING
3. STOCKING
4. ATOMIZATION
5. PRESSING / FORMING



The **ceramic mixture**, before the forming phase (during which the atomized powders are pressed or compacted), undergoes to a wet grinding process that involves the use of ground water (recovery water and groundwater).

During this step that is developed by means of Alsing type mills, the **ground water** together with the inorganic raw materials, forms the slurry that is also called barbottina.

Once it has been grinded, the slurry is usually sieved and stored in tanks within which it remains under constant stirring to avoid gelling and/or sedimentation phenomena.

After the storage phase – whose duration can range according to manufacturer's needs – the process goes on with the **atomization** by means of spray dryers (also called atomizers). Inside the atomizer the barbottina is nebulized by using very high temperatures, able to violently evaporate the water content. This evaporation turns the droplets of the slurry into tiny **hollow spheres** that form the atomized powder, ready for the pressing/forming phase.



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- **FEATURES OF ATOMIZED POWDER**

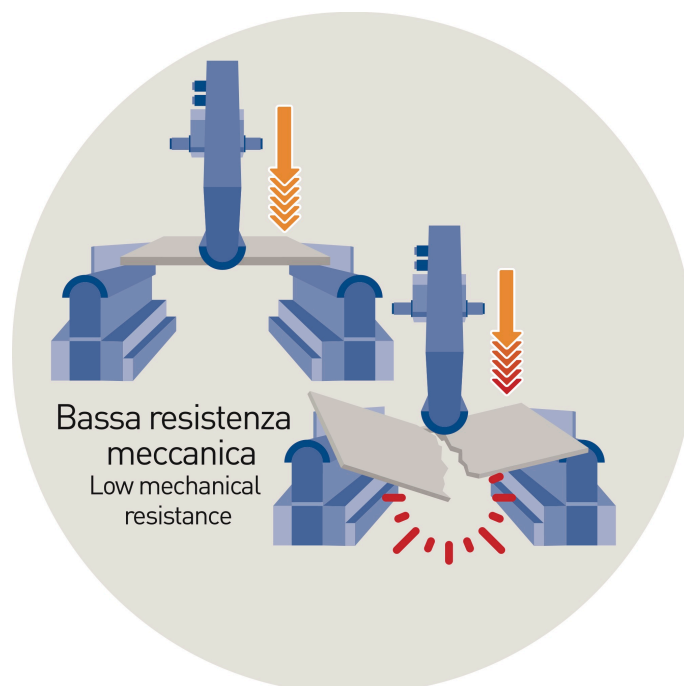
Despite the evaporation process that takes place inside the atomizers, the atomized powder retains a **residual moisture content** (usually 5/7%) that is useful to provide the granules with the proper plasticity value, to ensure their deformation during the pressing/forming process.

Once it has been pressed, the raw tile is, in fact, also called *green*, since it still contains a small amount of residual humidity (just like freshly cut wood).

3. CERAMIC MIXTURES AND MAIN CHEMICALS' CATEGORIES

Generally speaking, the use of organic and inorganic chemicals is very important (a must) - in all five stages described above - for the proper production of high performing ceramic material.

A) MECHANICAL RESISTANCE AND TEMPORARY BINDERS



If on the one hand the **residual humidity** provides the atomized powder with the right plasticity value, on the other, it can cause or lead to a **low mechanical resistance of the green tile**.

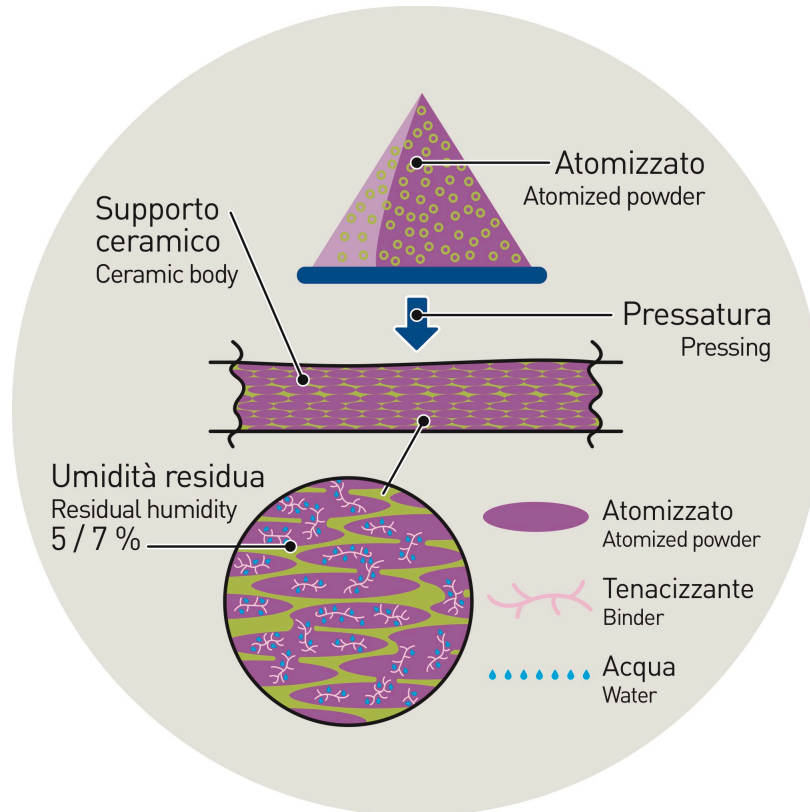
In fact, only after the drying and evaporation process that takes place inside the dryers, raw tiles gain a higher mechanical resistance.

More specifically, when the water leaves both the surface of inorganic particles and the surface of organic binders' molecules, the inorganic molecules (clays, in particular) approach and interact by means of molecular attractions, becoming harder and gaining a higher mechanical strength.



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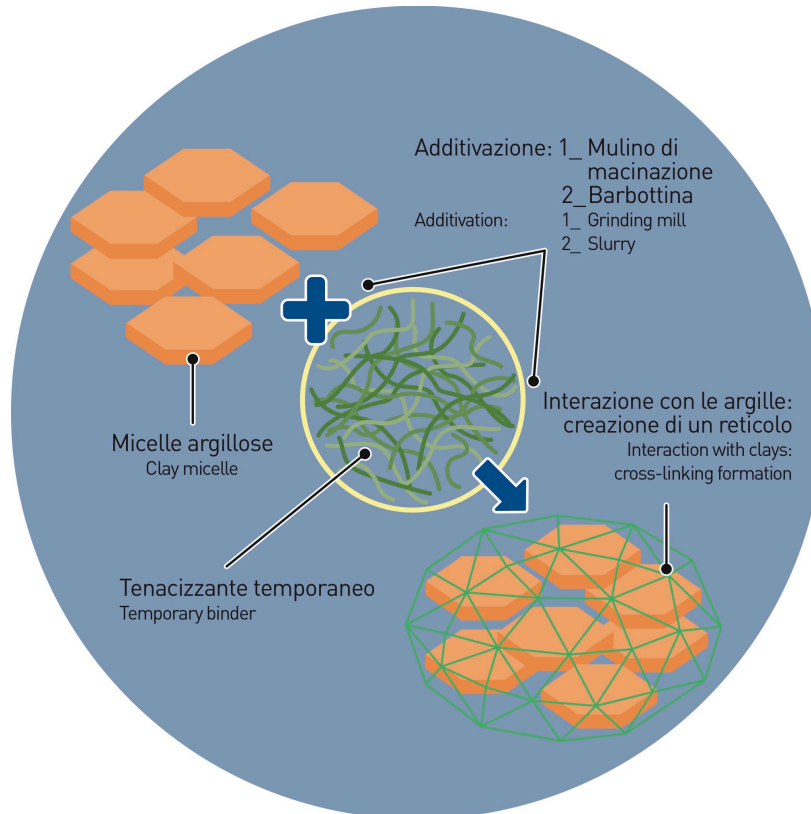


If we also consider the technical and aesthetic evolutions of ceramic tiles in the last years – big slabs and thin thicknesses – the tensions and mechanical resistance of raw tiles have become an important topic of discussion for all those who have to preserve the raw material from cracks and/or breakage.

In this respect, a lot of studies are currently underway on **organic raw materials and chemicals for ceramic mixture**. The formulation of the latter, and more precisely of **TEMPORARY BINDERS**, has now to take into consideration mechanical stresses that are completely different from those that usually occurred on small tiles. In the past, in fact, the **modulus of flexural strength** was the most important value to check, since the raw material was subjected to the compression of the rollers of the screen-printing decoration systems.

Today, instead it is more important to study and check other parameters, such as the **resistance to deformation, the resistance to impact or the cohesion of the product** (especially if it undergoes to a grinding or to a raw cutting processes).

Among the various options, the use of **temporary binders** is the most effective to increase the mechanical strength of ceramic dried tiles. They are so called because they bind the raw tile only during the pre-firing phase, preventing possible damages.



WHAT IS A TEMPORARY BINDER?

Binders are usually organic molecules able to promote a binding action with regard to the raw materials of the mixture, especially with clays.

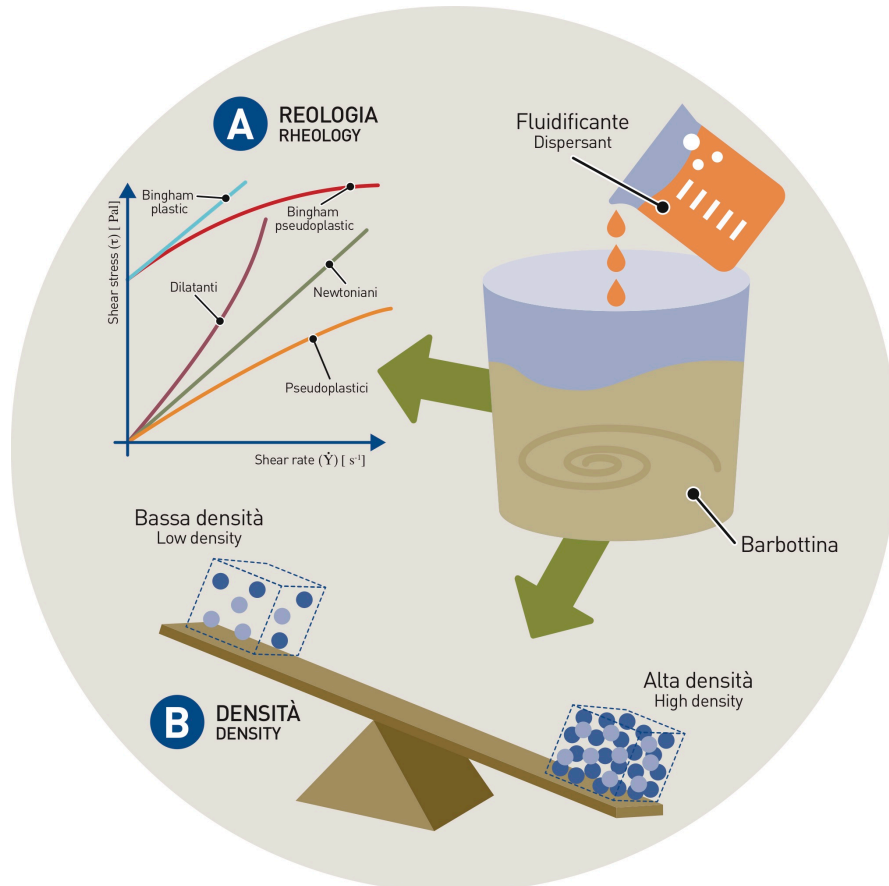
What happens from a chemical point of view?

A molecule of temporary binder contains functional groups (parts of the molecule able to chemically interact with other materials) that “**create a bridge**” both between the micelles and the hard inorganic raw materials. It basically links together the inorganic particles producing a crosslinking net that increases the resistance of the tiles after drying.

The temporary binder is usually added inside the mills during the raw materials' wet grinding process or directly inside the slurry (the mix of clays, raw materials and water).

B) ORGANIC ADDITIVES AND DISPERSANTS

In general, the grinding of a ceramic mixture without proper **DISPERSANTS**, besides several other problems, does not allow you to get a slurry marked by a **proper rheology** and a **high-density value**, two important or even fundamental aspects for the industrial productivity.



Let's go step by step and start from the process water used for grinding, a very important element for a proper fluidization.

- **Grinding waters: role, implications and dispersants**

The grinding water, that affect and that is essential to get the proper rheological values and to provide at the same time the ceramic mixture with a high-density, is generally composed of **well water and process water** usually deriving from the polishing and glazing departments, and sometimes from the cutting and sanding departments [the rate of well water compared to that of process water is different for each ceramic company and it changes according to the parameters in use].

The milling waters plays a decisive role for the proper development of the processes and they are fundamental to get high-performing ceramic products. To do this, they must be marked by specific features without which the whole process could be compromised, requiring the intervention of targeted additions.

What kind of features must the grinding water have?

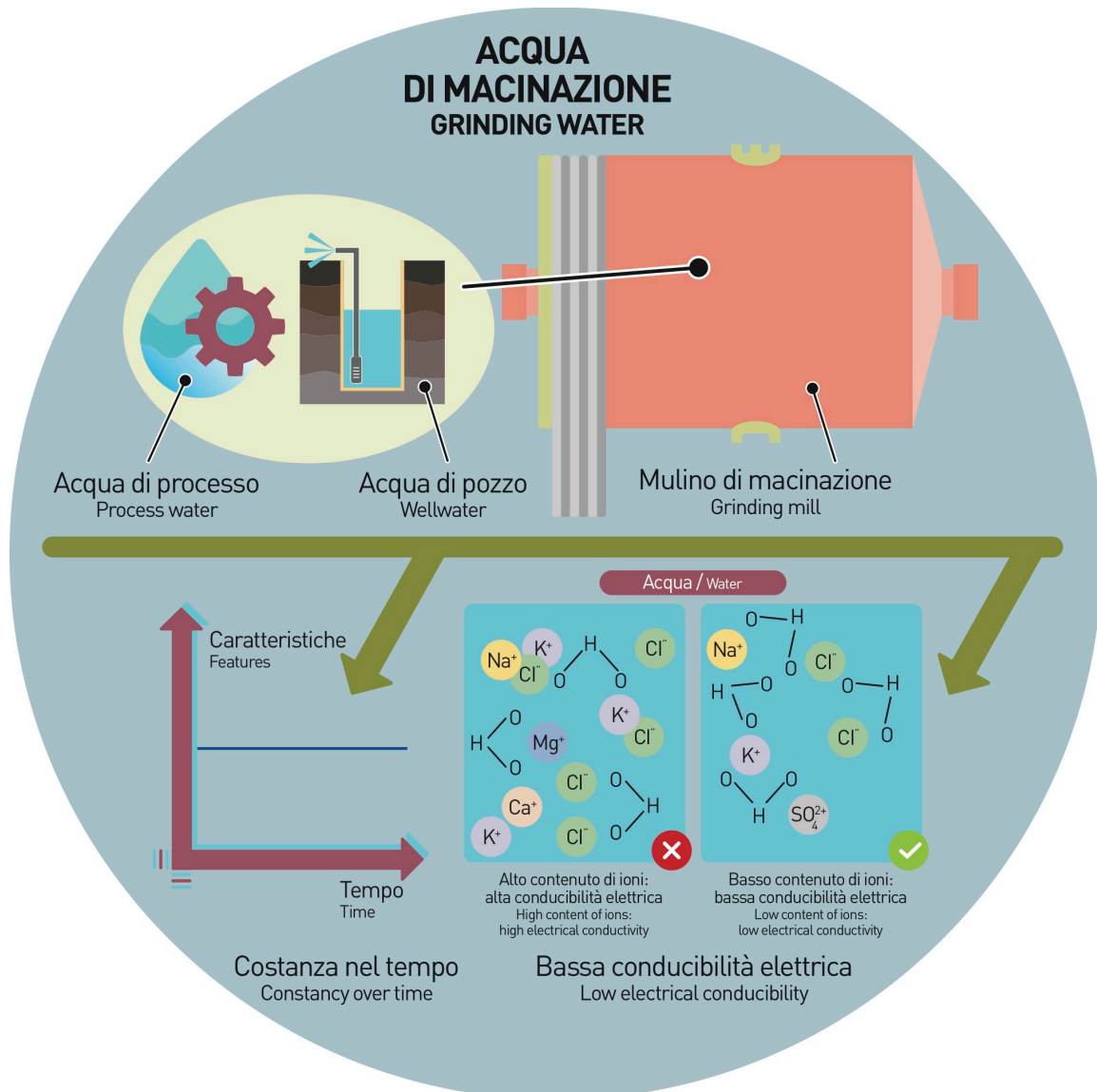
In general, the **composition** and the **quality** of the water must be **constant** over time, to avoid possible fluctuations in the milling parameters that would force the companies to continuous



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adaptations and modifications of production scenario. For this reason, they must undergo to constant controls, especially in terms of pH and **electrical conductivity** that provide a useful indication about the amounts of ions (cations and anions) in the water.



The **electrical conductivity** of the ground water **must be low or, even better, very low** in order to facilitate the fluidization process.

What does that mean (and why)?

To put it simply, a water marked by a low electrical conductivity is a water that contains a low concentration of ions.

An important quantity of multivalent anions and cations (such as calcium 2+ or magnesium 2+) can lead to significant problems to the fluidization process, reducing the thickness of the **diffuse layer**

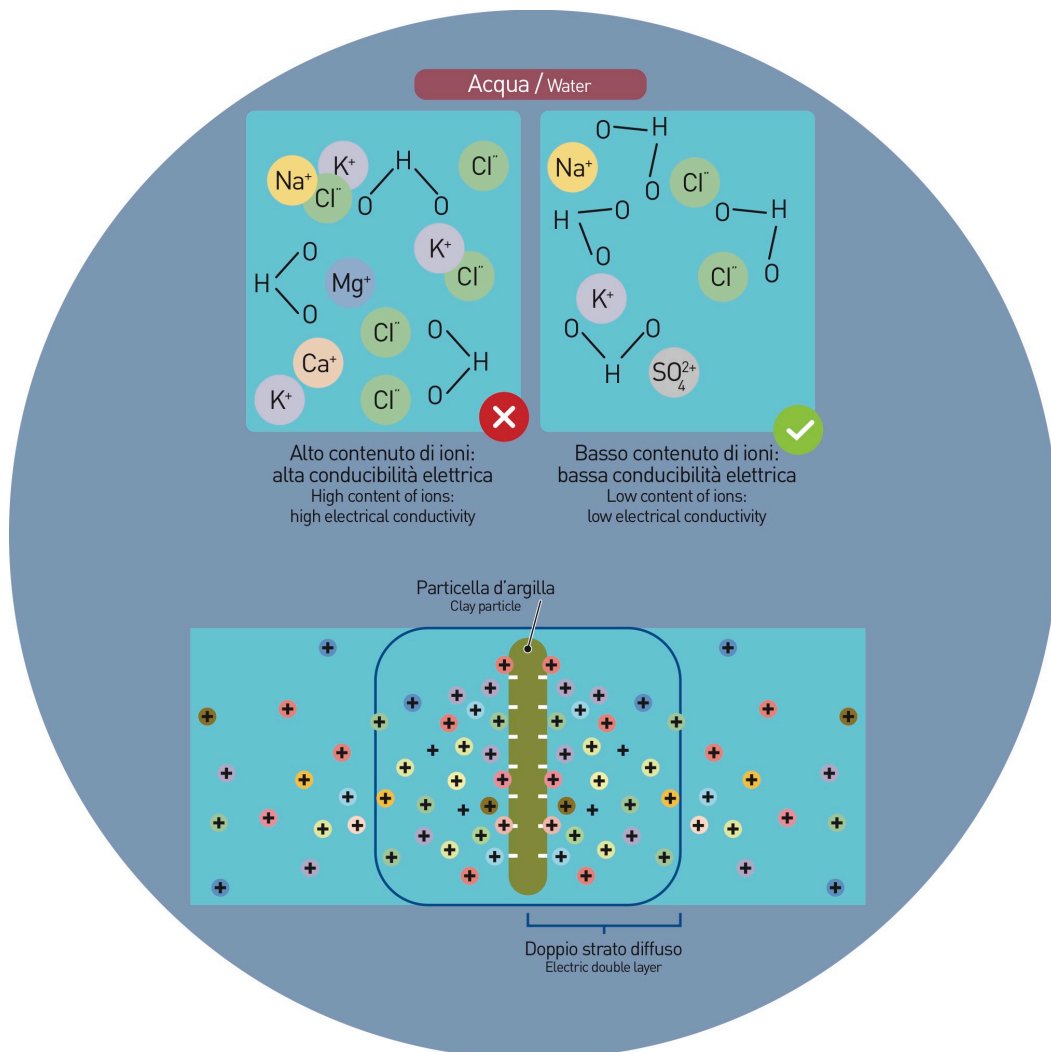


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on the surface of the clayey micelles, that is the distribution and thickness of anions and cations on the surface of the clay micelle.

This reduction results in a general higher viscosity of the system (barbottina) due to the presence of electrostatic attraction phenomena. We could say, a bit simplistically, that the solid parts of the suspension (the micelles) attract by increasing the viscosity of the suspension.



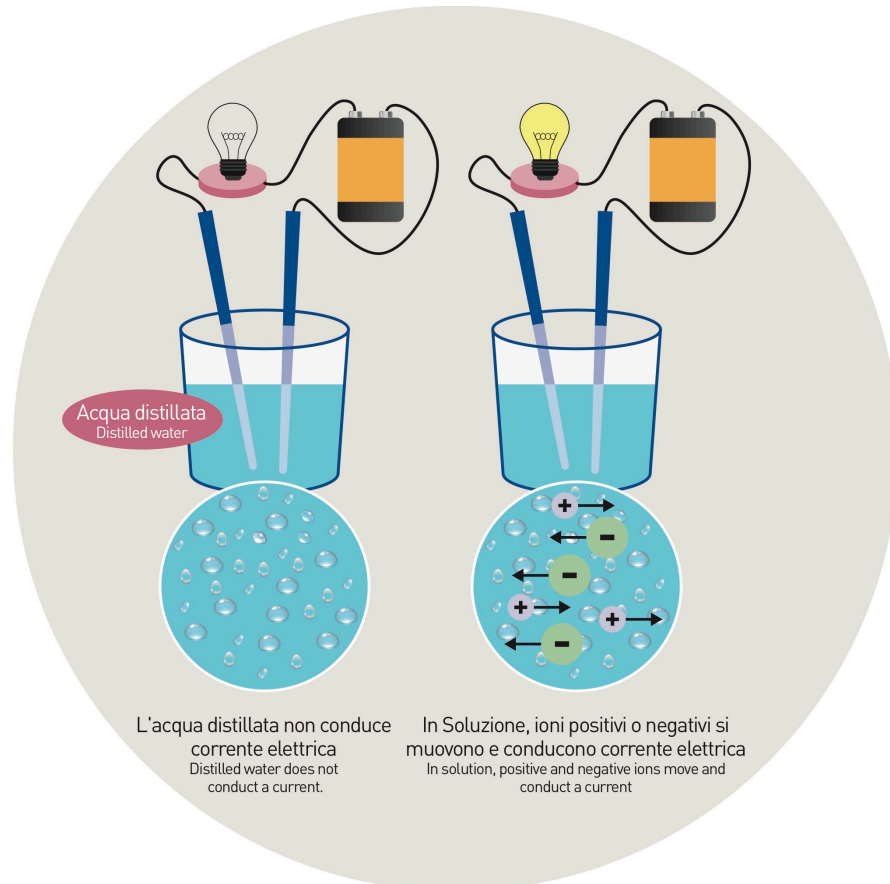
In other words:

an excessive amount of ions (whether monovalent or multivalent) together with a water low content can increase the viscosity: the ions begin to interfere between the diffuse layers of clay micelles and the only way to stop their interaction (and thus the problem) is to add water to the system to lower the ionic concentration level.



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In electrochemistry, the diffuse double layer (or electric double layer) consists of a structure that originates at the interface solid-liquid, at which a transfer of electric charge occurs, along with oxidation-reduction half-reactions.

From a chemical point of view:

Under the same condition of electrical conductivity, the presence of ions in the milling water (especially **monovalent** cations) facilitates the milling process compared to the same water containing cations or **multivalent** ions.

On the contrary, a low quantity of ions (both monovalent and multivalent) in the grinding water allows the micelles to fluidly glide one over the other, avoiding phenomena of attraction and so of viscosity increasing. (A significant amount of ions - and therefore a water marked by a high conductivity - is able to reduce the "availability of water" within the system, worsening its fluidity). It is now clear why the little water content of the barbottina must be characterized by a low conductivity, even more if we consider that the challenge of all ceramic producers is today to increase the slip density (by reducing the water content as much as possible) to increase and improve the productivity, by decreasing the energy costs required for the water evaporation process.



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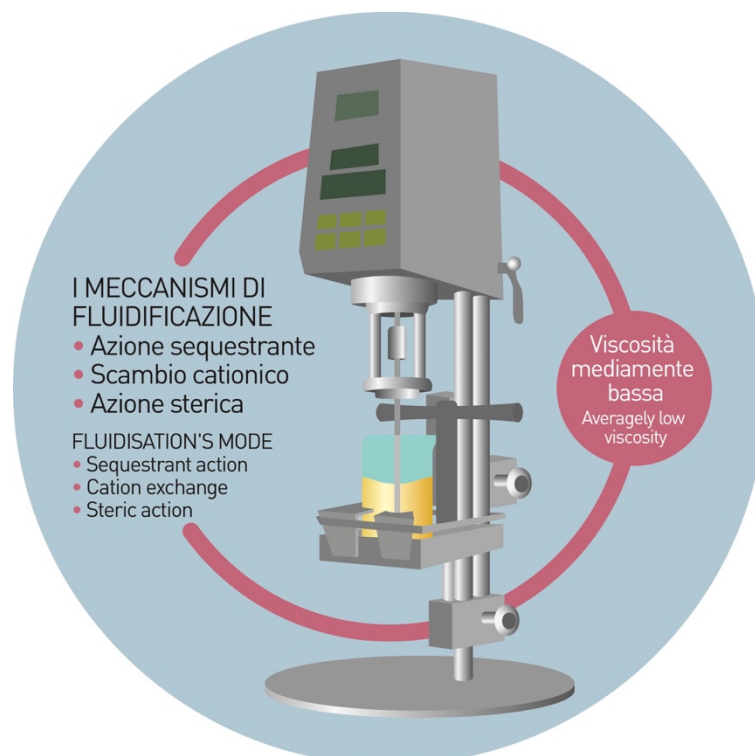
- **The dispersants' role**

To avoid defects resulting from the water's high conductivity by using chemicals is very complex. However, the use (during the milling process) of suitable **dispersants that act with a sequestrant action** against bivalent or multivalent cations can certainly reduce possible defects and facilitate the process.

Dispersants for ceramic mixture are all ionic, sodium salt, and they are usually developed to carry out all the following fluidization mechanisms:

- Sequestrant action
- Cationic exchange
- Steric action

The ceramic mixture is an extremely heterogeneous and complex system, and this is why during a fluidization's study it is important to evaluate different types of molecules to optimize both the cost of fluidification and the barbotina's working density.



Generally speaking, a ceramic mixture's fluidization is ideal when the rheology of the system provides, during the milling phase, an average low viscosity that can reduce the energy consumption and the milling times.

All chemicals involved must lead to a not too fluid and not overly viscous ceramic mixture: both scenarios would negatively impact on the Alsing grinding system, making it not performing.



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It is important to point out that all features of the barbotina's rheology - from grinding to storage - are simulated and reproduced within the labs by using proper programs provided by the **rheometers**.

FOCUS: THE RHEOMETER

The rheometer is a lab tool used to measure the flow of a liquid (a suspension) in response to the application of specific forces. It is used for those fluids that cannot be defined only for their viscosity value (in which case a viscometer would be used) but that need more complex analyses that take into account different parameters. In other words, the rheometer measures the rheology of a fluid.

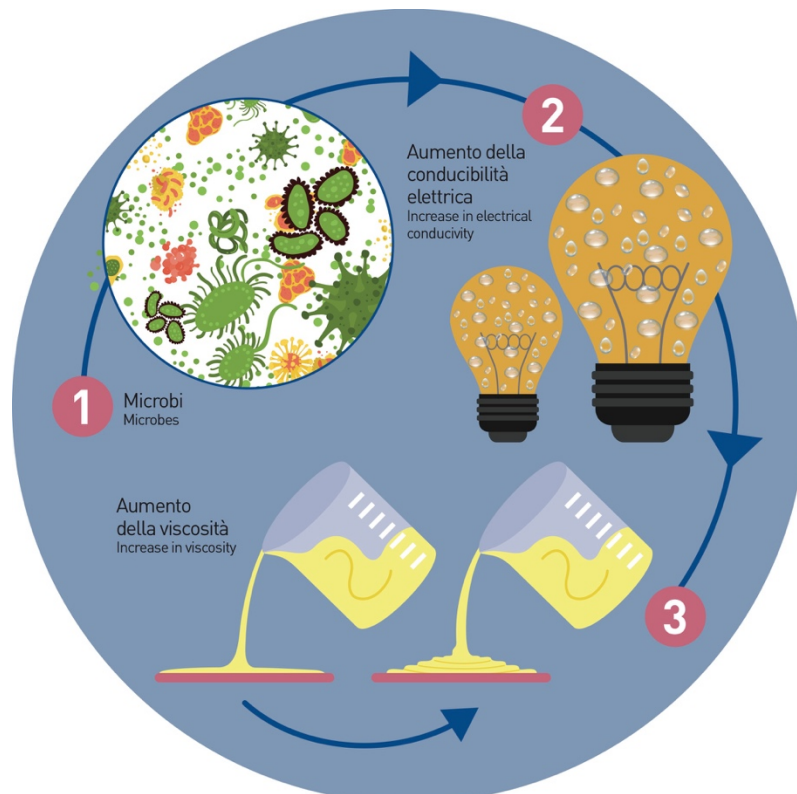
C) SANITIZING & PRESERVATIVES

Microbiologic degradations:

increasing of the electrical conductivity and therefore of the system's viscosity

The trend of the **electrical conductivity** can also be affected by microbiological degradation phenomena of process waters that always contain concentrations of **organic material**.

Microbiological degradation of organic molecules, that involves the formation of many metabolites (waste produced by micro-organisms), can sometimes increase the electrical conductivity value. This leads in turns to an increase in the ionic charge of the barbotina that, together with other elements, increase the viscosity of the system.





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- **Monitoring**

The importance of constant monitoring of process and milling water to prevent any possible complications is quite clear.

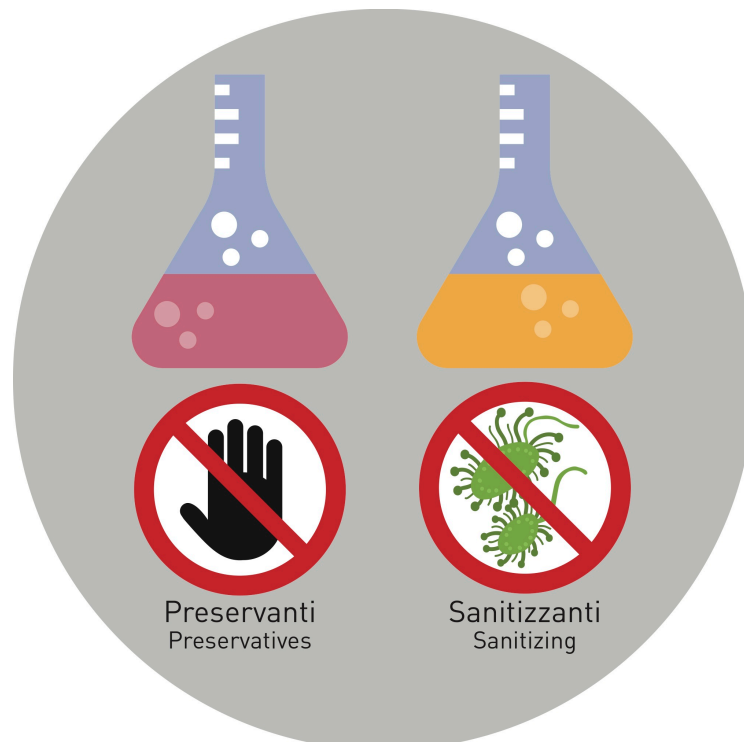
Especially in the warmer and wetter seasons, it would be useful to carry out in-depth studies of the water cycle within the production plant, identifying the most sensitive storage points and intervening with appropriate periodic sanitisation procedures and dosage (constantly over time) of appropriate preservatives.

- **Additives for process waters**

Even in these cases, the only possible action is the addition of water to restore mobility to the system. However, it is also possible to take preventive actions to avoid degradation phenomena by using specific **chemicals capable of sanitizing and preserving** water: products capable of killing micro-organisms and/or avoiding their proliferation over time.

We are talking about **SANITIZERS** (usually oxidizing products) when these products have a rather fast action with short-term effects on microorganisms: Microorganisms are eradicated but bacteria can reappear in short times.

We speak of **PRESERVATIVES** in the case of molecules that can react over time within the water, ensuring its health.





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In any case, it is important to take actions in the preliminary stages of the entire process to avoid an increase in conductivity (promoted by the degradation). The addition of these chemicals only in the milling phase would be late and therefore ineffective.

Why are sanitizers and preservatives usually used in combination?

The **preservative** ensure that the water without bacteria does not undergo to degradation phenomena: any bacterial colony (or spore) that may occur is, in fact, neutralized.

The **sanitizer** guarantees, in case of uncontrolled microorganisms' proliferation, the complete removal in a short time.

D) ADDITIVES FOR BLACK CORE REDUCTION

Check stop #16 (video and pdf) for information on the topic.

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