

# Mechanisms of action of deflocculants and dispersants in ceramic bodies

## **Mechanisms of action of deflocculants and dispersants in ceramic bodies**

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## 1. Introduction

The preparation of ceramic bodies via the slip phase offers the advantage of optimal dissolution and good homogenization of the raw materials. A further argument for liquid preparation is the lower energy requirement for wet milling when compared with dry milling. However, in order to reduce the higher energy costs for the subsequent dewatering by spray drying as much as possible, it is necessary to achieve high solids contents. In addition, it is necessary, for reasons of production technology, to adjust rheological properties in a controlled manner and to guarantee slip stability over time.

Ceramic slips are dispersions. These dispersions contain finely divided solids in a liquid medium. Solids in ceramic slips consist of silicate ceramic, oxide ceramic, and non-oxide ceramic raw materials. The dispersant will be assumed to be water in the following explanations.

Gravity and electrostatic forces make the solids particles in these systems agglomerate and sediment. In order to prevent agglomeration, i.e., to stabilize the slip, it is necessary to arrange for optimal repulsive forces to act between the solids particles. Here, the addition of suitable deflocculants and dispersants makes it possible to exert a controlled influence.

### **1.1. Definition of rheological terms**

Rheology is concerned with the deformation and flow properties of substances under the influence of external forces. In order to define the rheological behaviour of a ceramic slip unequivocally, it is necessary to use the relevant concepts in a uniform manner. The most important notions will, therefore, be described here in brief.

The viscosity of a ceramic slip is a measure of the internal friction between the molecules of the dispersion. The constant of proportionality of the ratio of the shear stress and the shear rate is the shear viscosity.

$$\eta = \frac{\tau}{\dot{\gamma}}$$

$\eta$	viscosity [mPa·s]
$\tau$	shear stress [Pa]
$\dot{\gamma}$	shear rate [1/s]

External forces, e.g., the shear forces produced on stirring a slip, influence the flow behaviour. This leads to variation in the behaviour as a function of the strength and duration of the external forces.

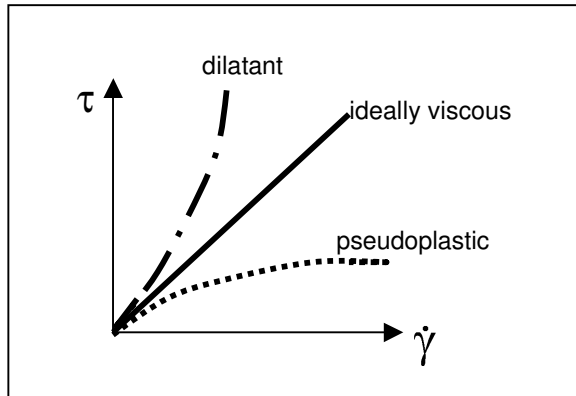
#### Newtonian flow behaviour

Here the shear stress produced by a shearing force is directly proportional to the rate of shear, hence this is ideally viscous or Newtonian flow behaviour. In general, the technological systems, such as ceramic slips, deviate from ideal flow behaviour.

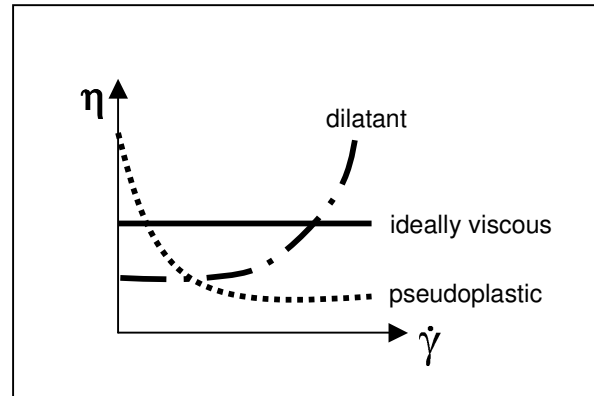
#### Pseudoplastic and dilatant flow behaviour

If a ceramic slip is subjected to increasing shear stress it exhibits pseudoplastic (structural viscous) or dilatant flow behaviour. In contrast to Newtonian flow behaviour, the ratio of shearing force to rate of shear is not constant in pseudoplastic or dilatant flow behaviour. A single point measurement of the viscosity is therefore not adequate to describe the flow behaviour of ceramic slips.

It is necessary to consider the whole flow curve as shown in figures 1 and 2.



**Fig. 1 Flow curves**



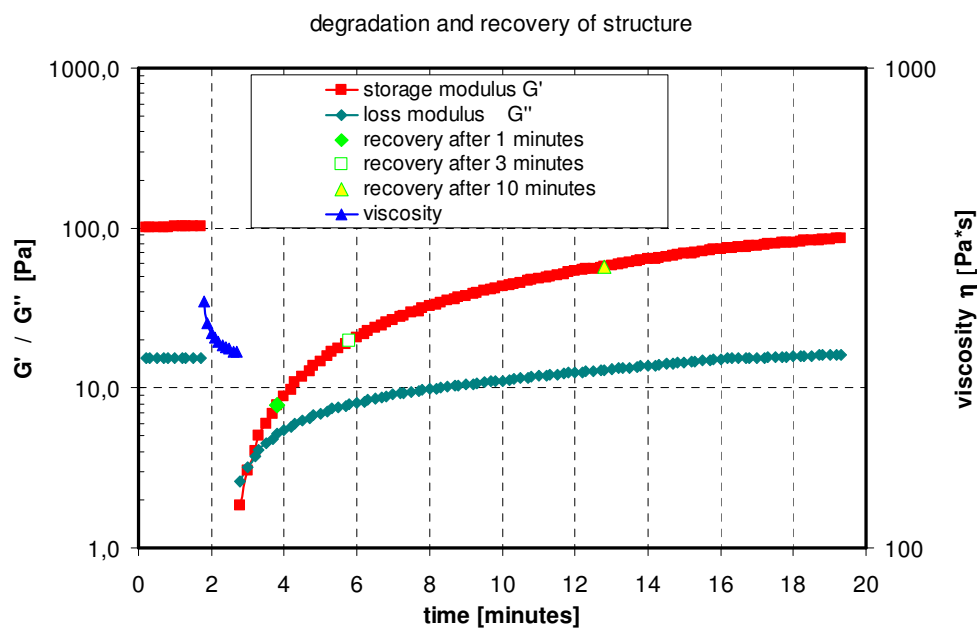
**Fig. 2 Viscosity curves**

In pseudoplastic flow behaviour the viscosity decreases with increasing shear force, in the case of dilatant flow behaviour it increases. The flow behaviour depends on the type of raw material used, its particle size distribution and particle shape, and the addition of deflocculants.

### Thixotropic and rheopexic behaviour

By thixotropic behaviour we understand the degradation of a suspension's structure during a stress phase and its complete rebuilt during a subsequent relaxation phase, i.e. the viscosity decreases under stress and will recover during relaxation. This process is reversible. Rheopexic substances behave in precisely the opposite manner.

Interval thixotropic-tests are often used to characterize the thixotropy by a rheometer ( rest interval / load interval / recovery interval ). To determine the relaxation phase as best as possible the measurements are generally carried out by an oscillating method. Figure 3 shows the degradation and recovery of a ceramic body's structure by means of such a step-test. Thixotropy can be influenced with the aid of additives.



**Fig. 3: Interval thixotropy-test (oscillation mode)**

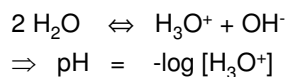
## **2. The water-solids-system**

The viscosity and rheological properties of a slip are influenced by every component of the water-solids-deflocculant system. An optimal deflocculation is only possible if each individual component of the system and the effects of interaction are considered. In the same manner, this also applies when searching for possible faults, when the properties of a system that is otherwise functioning deviate.

The starting point for the optimization of slip properties is the water-solids system. In the following, these two components will be considered separately as well as in interaction in order to illustrate the relations which are relevant for deflocculation, and the selection of the correct deflocculant.

### **2.1. The parameter „water“**

The water used in ceramic technology generally contains dissolved salts as a natural component. These influence the dissociation equilibrium that is set up, and, hence, the ions present in the dispersion. The dissociation equilibrium is defined by the pH as well as by the concentration of the dissolved ions. The following dissociation equilibrium is set up in electrolyte-free water at neutral pH:



If the water contains soluble salts, a dissociation equilibrium is set up with the interaction of other ions, e.g.  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ . Depending on their type and their proportion the ions present interact with the water and with the solids particles of a dispersion.

The bivalent cations, calcium and magnesium, contained in the dissolved salts, interfere with deflocculation. The more of these cations present the greater is the degree of hardness of the water. Here one degree = 10 mg CaO / 1 l water. The harder the water the more complexing agent is required or a more effective one must be selected in order to bind these cations.

If the  $\text{pH} \leq 6$ , these cations are bound and have no effect on the deflocculation. If there is an excess of  $\text{OH}^-$  ions, that is a  $\text{pH} \geq 7$ , then it is necessary to complex the calcium or magnesium ions in order to yield optimal slip properties with high solids content. The bonding of these cations by complexing agents is discussed in more detail under Section 3.1.3.

### **2.2. The parameter „solids“**

Solids are characterized by mineralogical, chemical and morphological parameters. The rheological properties of their dispersions and the starting conditions for an optimal deflocculation depend on the state of the solids.

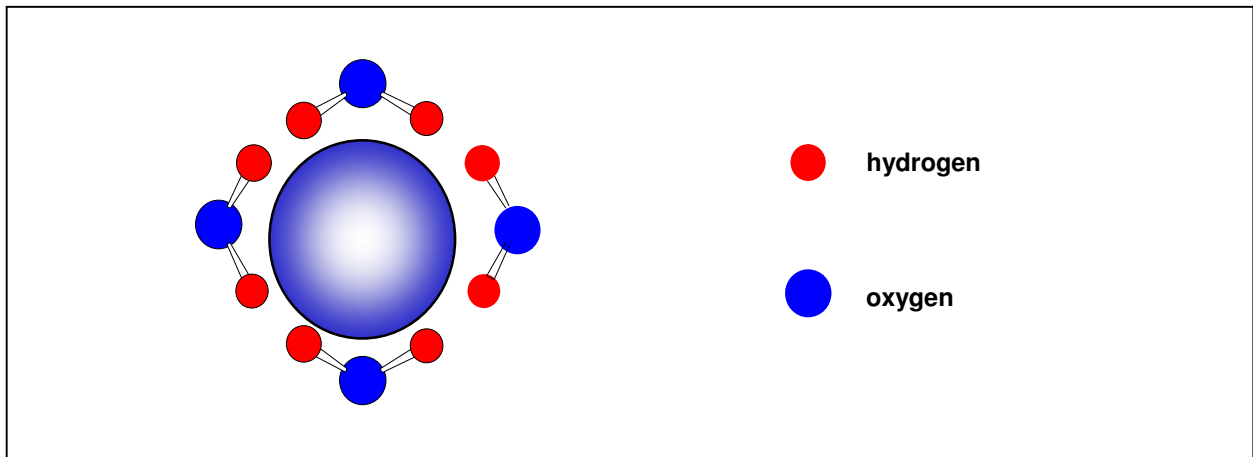
The sedimentation tendency, the specific surface and cation exchange capacity are all influenced by the size and density of the particles. The sedimentation tendency increases with increasing particle size and particle density. If the specific surface increases, the energy of the whole system also increases, so that the tendency of smaller particles to agglomerate is greater.

The surfaces of solids are interfaces in an unsaturated bonding state. The outermost layer is composed of  $\text{O}^{2-}$  ions. These ions originate either in the structure of the crystal itself (silicate ceramic and oxide ceramic raw materials) or result from taking up oxygen from the atmosphere (non-oxide ceramic raw materials). The mechanical destruction of the solids, e.g. during milling or under great shear stress, also produces surfaces that are unsaturated. These free bonds, which are created on fracture, also have a powerful tendency to saturate. The compensation of these unsaturated bonding sites occurs by hydration - the addition of  $\text{H}_2\text{O}$  molecules - in aqueous systems.

**2.3. Characterization of solids surfaces in the water-solids system**

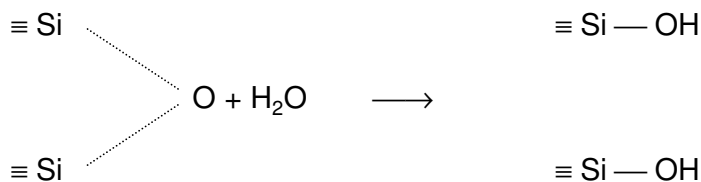
**2.3.1. Hydration**

The molecules of water act as dipoles and are attracted by ions. The smaller the ion the larger is its effect on the water molecules and the more strongly a certain number of water molecules will be immobilized at the ion. This also applies when we consider the anionic surfaces of ceramic raw material particles, as is shown schematically in Figure 4.



**Fig. 4: Hydration of a negatively charged particle**

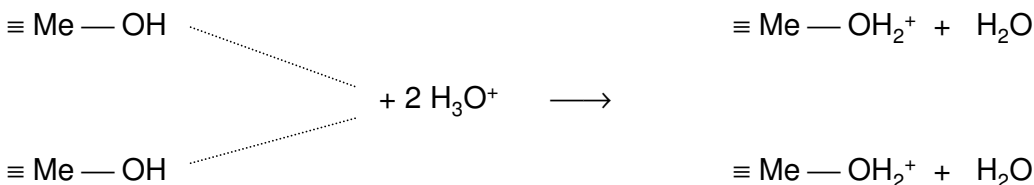
For example,  $\text{Si}^{4+}$  reacts as follows on contact with water:



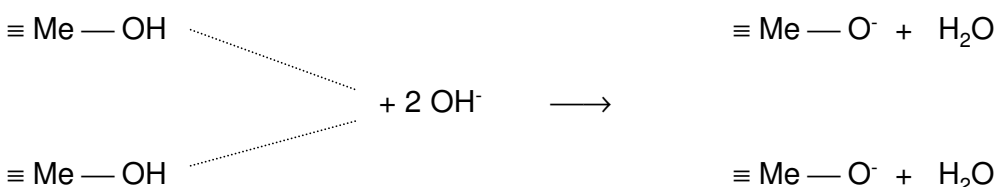
**2.3.2. pH-dependent interactions**

The following pH-dependent interactions between ceramic particle surfaces (Me-OH surface groups) and water follow as a result of hydration. Me represents, for instance, Si.

**a positive surface charge results in the acidic pH range:**



**a negative surface charge results in the alkaline pH range:**



From the scheme it is evident that the resulting surface charge on the raw material particle is dependent on the pH of the water used as dispersion medium, i.e. it depends on whether there is an excess of  $H_3O^+$  ions or of  $OH^-$  ions.

The case where the surface charge, that results, is negative, i.e.  $pH \geq 8$ , is relevant for the deflocculation of ceramic raw materials. This ideal pH range for the optimal stability of a slip can be deduced from arguments set out in Figure 5. In the case of silicate raw materials this occurs because of the differing surface charge of the particles as a result of diadochic replacement of ions in the silicate lattice. Silicate ceramic raw materials have disturbed lattices, i.e.  $Si^{4+}$  is replaced by, for example,  $Al^{3+}$  or  $Al^{3+}$  by, for example,  $Mg^{2+}$ , so that excess negative charges occur at the edges of clay mineral platelets. The variation in charge, which is also represented in Figure 5, results in a variation in the spatial configuration of the particles in the water-solids system.

It can be seen from the figure that the spatial structure existing in alkaline medium is most favourable for the long-term stability of a slip with a high solids content.

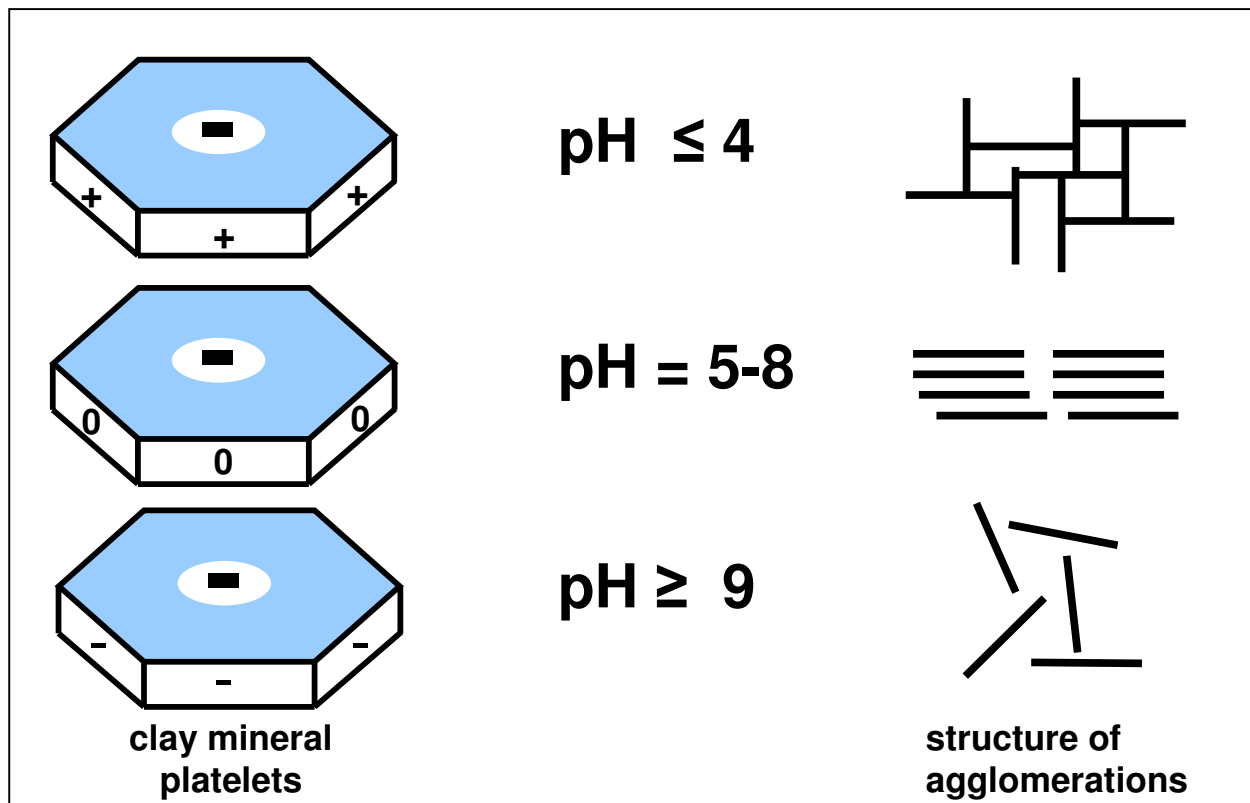


Fig. 5: Charge distribution

### 2.3.3. Formation of the electrical double layer

An electrical double layer, with corresponding zeta potential (red curve), will form in the water-solids-system, depending on the surface charge of the solids particles. This is shown in Figure 6.

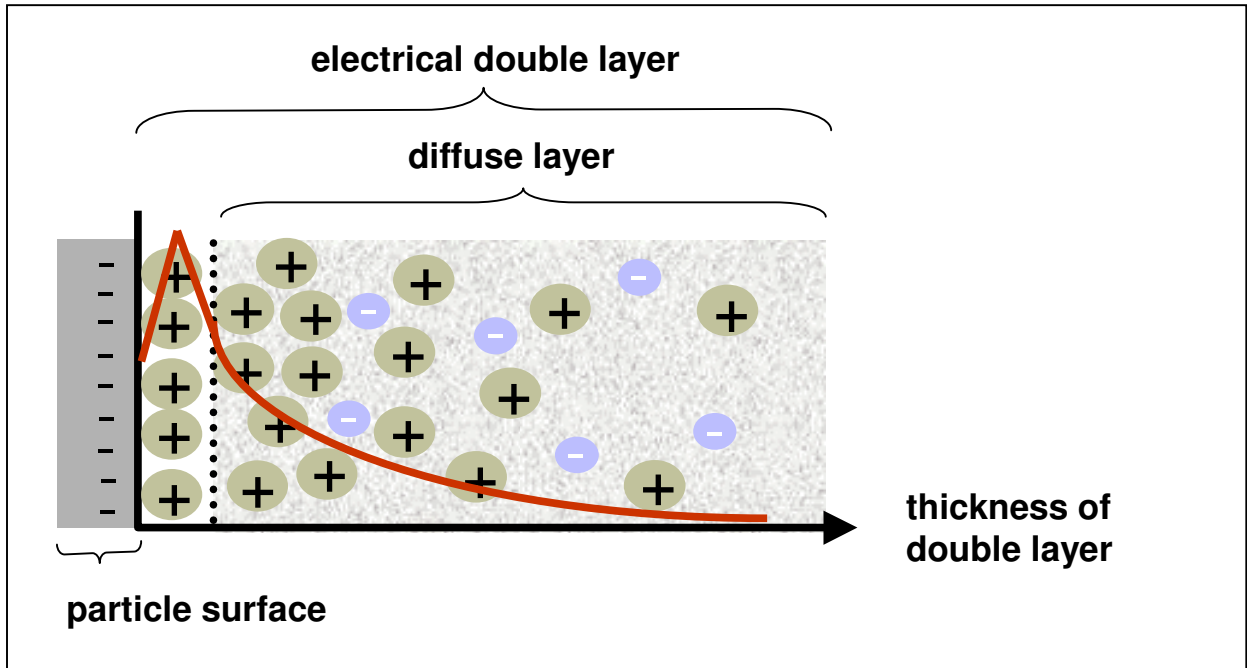


Fig. 6: Electrical double layer with variation of zeta potential

It is not only the resulting surface charge of the particles which is decisive for the arrangement of the particles in the dispersion, it is also the charge density. Figure 7 schematically illustrates the differing thicknesses of the electrical double layer at varying charge densities.

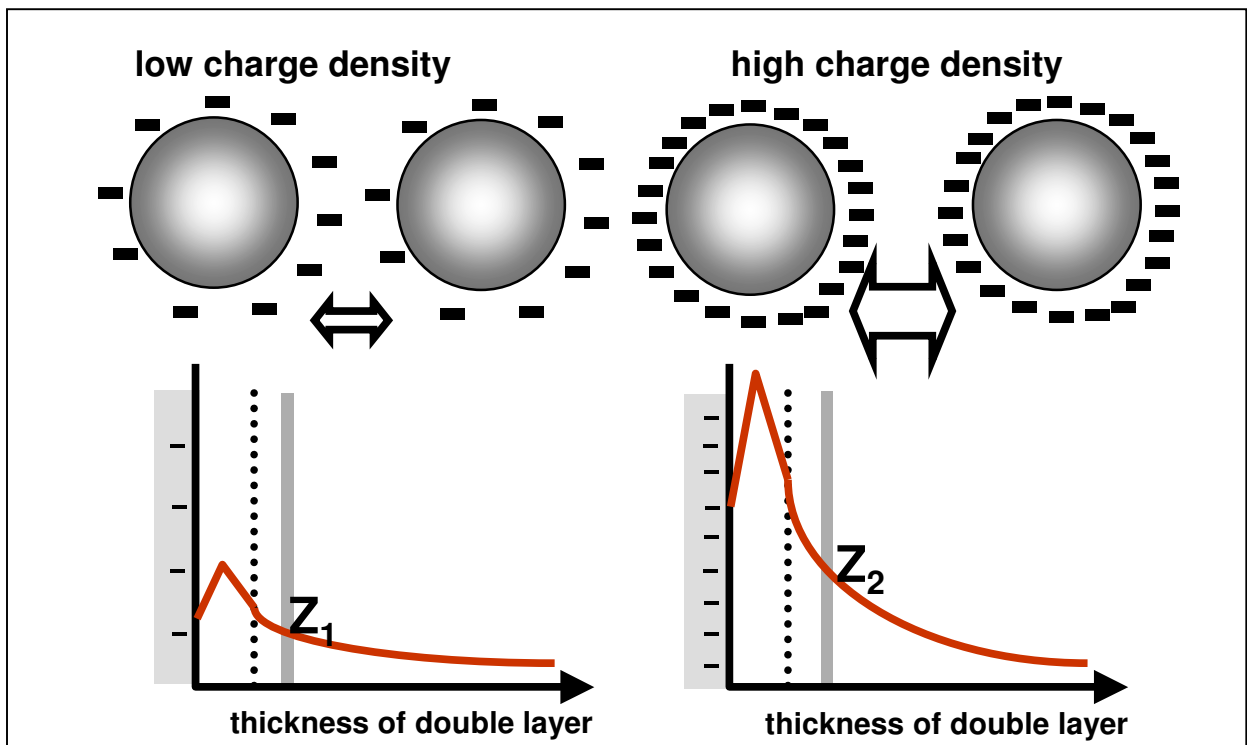


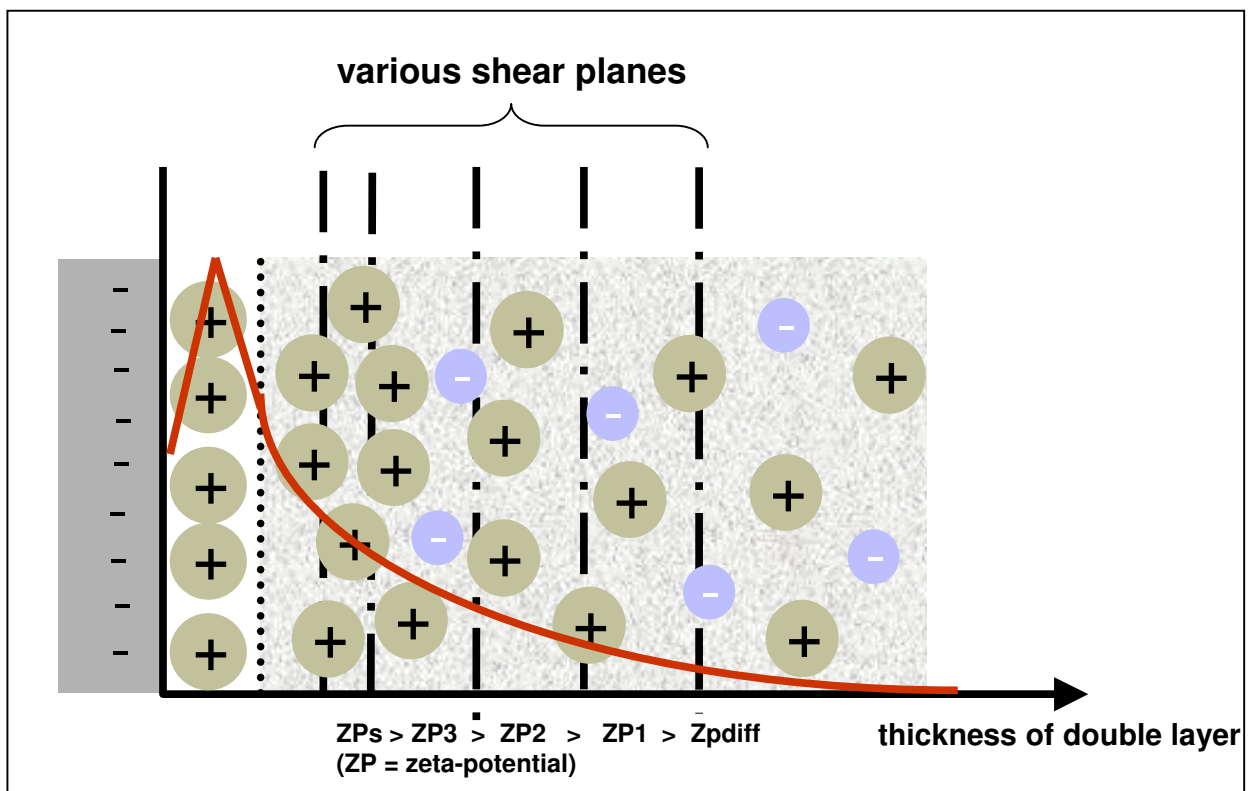
Fig. 7: Formation of the zeta potential ( $\zeta$ ) at varying charge densities

The charge density is a function of the structure of the solids. The charge that results depends on the degree of irregularity in the lattice structure of the raw material. The higher the charge density the higher the thickness of the electrical double layer. Natural raw materials, as used in silicate ceramics, have highly irregular lattice structures and, hence, a high charge density on account of the impurities they contain. Therefore, there should be a large repulsion potential.

On the other hand, the coating of the particle surfaces with bivalent cations in the water-solids-system leads to the formation of a relatively thin electrical double layer, since these cannot completely shield the negative surfaces of the clay minerals. Agglomerates of various degrees of stability occur as a result of the effects of attractive forces.

The electrical double layer is also affected by shearing forces when the slip is stirred. It can be assumed that this stress shears off a part of the diffuse layer.

When the variation of the zeta potential within the electrical double layer is considered, it becomes evident that differing zeta potentials will occur depending on the depth to which this shearing occurs (see Fig. 8). These varying potentials also necessarily require different saturations in order to set up adequate repulsion forces between the raw material particles.



**Fig. 8: Formation of shear planes and differing zeta potentials as a function of shear stress**

### 3. The water-solids-deflocculant-system

As described, the agglomeration, which interferes with high solids content and optimal rheological function, is brought about by attractive electrostatic forces. The purpose of deflocculants is to increase the distance between the raw material particles and, hence, to inhibit agglomeration by influencing these electrostatic forces. Since the strength of these attractive forces is influenced by the characteristic properties of water and solids described above, it is necessary to add varying quantities and to combine the mechanisms of action of the deflocculants, in order to bring about optimal deflocculation for every composition.

#### 3.1. Mechanisms of action in the water-solids-deflocculant system

There are basically three mechanisms which act individually or in combination depending on the deflocculant used:

- cation exchange and, thus, an effect on the thickness of the electrical double layer of the raw material particles
- steric repulsion by the introduction of functional groups, which act as spacers between the raw material particles
- binding of interfering cations by complexing

##### 3.1.1. Electrostatic repulsion by cation exchange

The formation of the electrical double layer was described in Section 2.3. In the two substance water-solids-system the double layers are thin as they take up bivalent cations from the mixing water. In order to enlarge the electrical double layer and, hence, to increase the repulsion effect, it is necessary to replace the bivalent cations with monovalent ones.

Figure 9 illustrates this process.

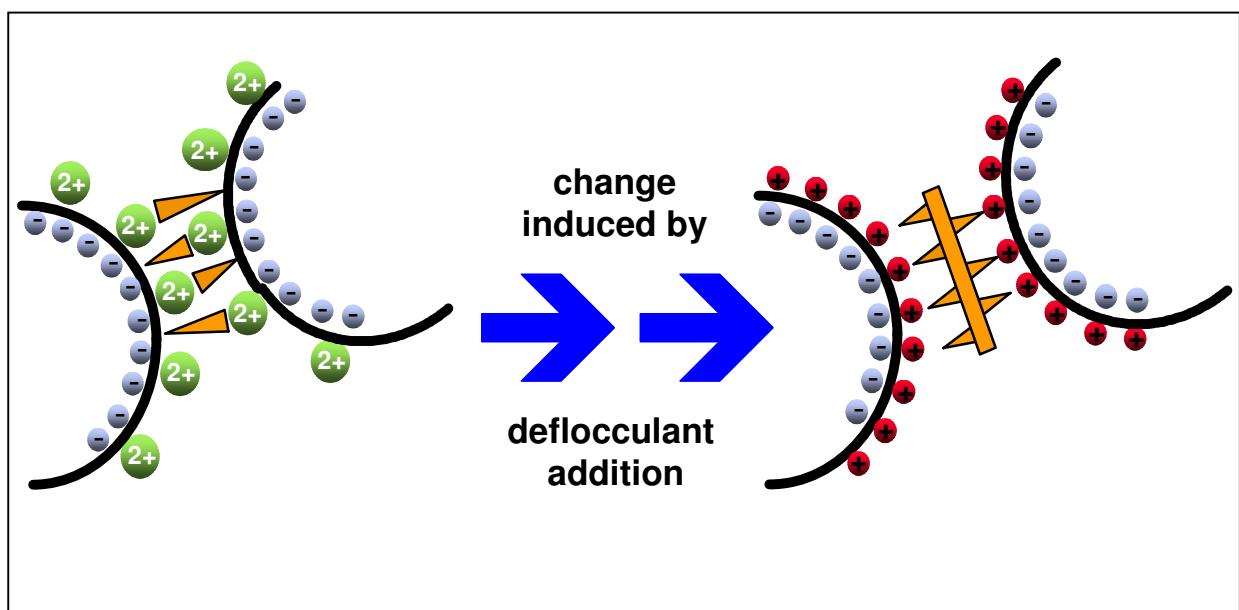


Fig. 9: Influence of cation exchange on the electrical double layer

The occupation with bivalent cations (calcium, magnesium) is illustrated on the left-hand side of the diagram. The negative surface charge of the clay minerals cannot be completely screened off here. The attractive forces predominate at this moment.

An exchange of the multivalent cations against monovalent ones (e.g. sodium) leads to better shielding and to an increase in the double layer as a result of the then externally neutral behaviour of the clay mineral particles and the primarily repulsive forces associated with this. Agglomeration of the particles is prevented and viscosity is reduced.

### 3.1.2. Steric repulsion

A steric repulsion is brought about by the use of dispersants with functional groups. These functional groups act as spacers between the raw material particles.

This process is illustrated schematically in Figure 10.

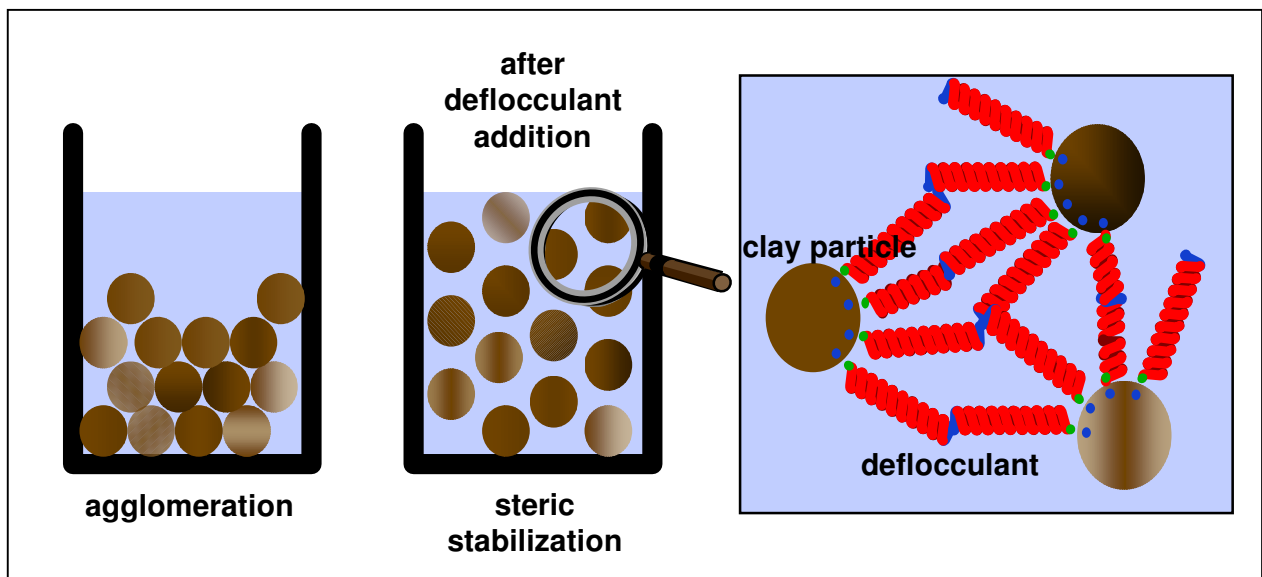


Fig. 10: Principle of steric repulsion

On the left-hand side of the diagram the particles in the aqueous dispersion have sedimented on account of gravity. The deposition of the dispersant on the surface of the raw material particles brings about a repulsive effect that leads to a uniform distribution of the fine particles in the dispersion in which all particles are ideally having the same distance from the nearest neighbouring particles.

In the enlarged cross section of the dispersion the effect of the deflocculant, a polymer with functional groups, is illustrated schematically. The functional groups interact with the particle surface by charge compensation. Here the positively charged "anchor" group of the additive attaches itself to negatively charged clay particle surfaces. Since the polymer chains of the additive contain functional groups with positive and negative charge, there are controlled attractive and repulsive effects. Hence, there is a targeted compensation of agglomeration tendencies.

### 3.1.3. Complexing

The presence of bivalent cations, from salts dissolved in the water, was pointed out in section 2.1. Consideration of the electrical double layers has shown that since they cause thin double layers, these cations interfere with deflocculation. Exchanging them for monovalent cations, as described in section 3.1.1, is a means of having an effect here. Another way is to add inorganic complexing agents, which bind free bivalent cations before they can become attached to the surface of the raw material particle. The complexing of these free multivalent cations (e.g.  $\text{Ca}^{2+}$ ) is illustrated schematically in Figure 11.

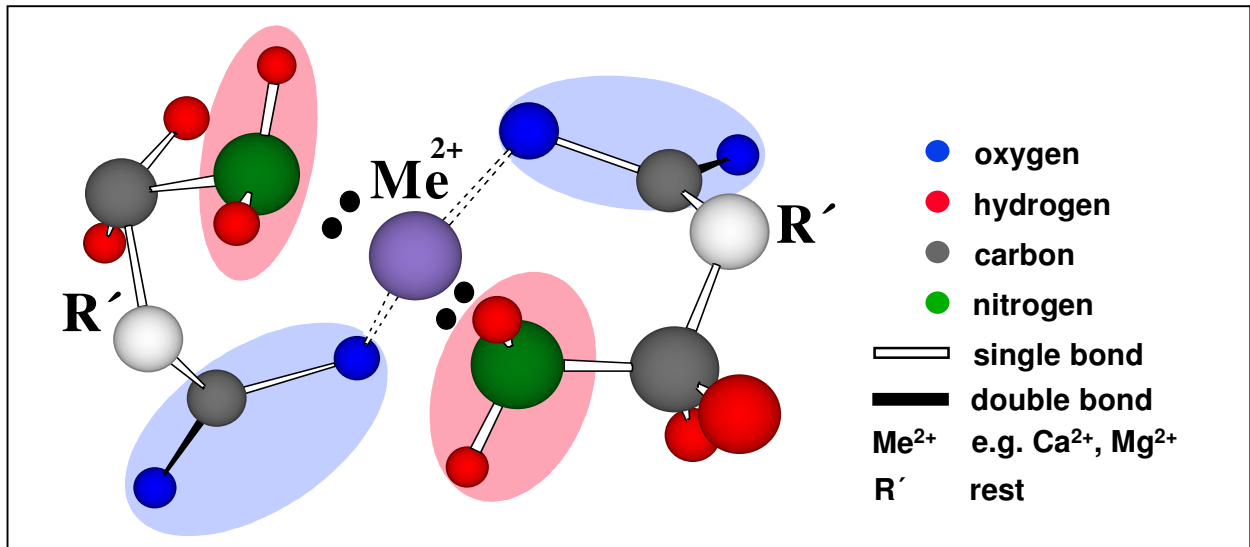


Fig. 11: Principle of complexing

Complexing agents contain functional groups (e.g. amine groups), that have free valences in their electronic shells. These valences are available for formation of electron pair bonds with free multivalent cations. This reduces or eliminates the influence of these cations on the electrical double layers of the clay minerals.

### 3.2. The raw material basis for deflocculants and dispersants

Figure 12 gives an overview of the most important raw materials used for the manufacture of deflocculants and dispersants by Zschimmer & Schwarz.

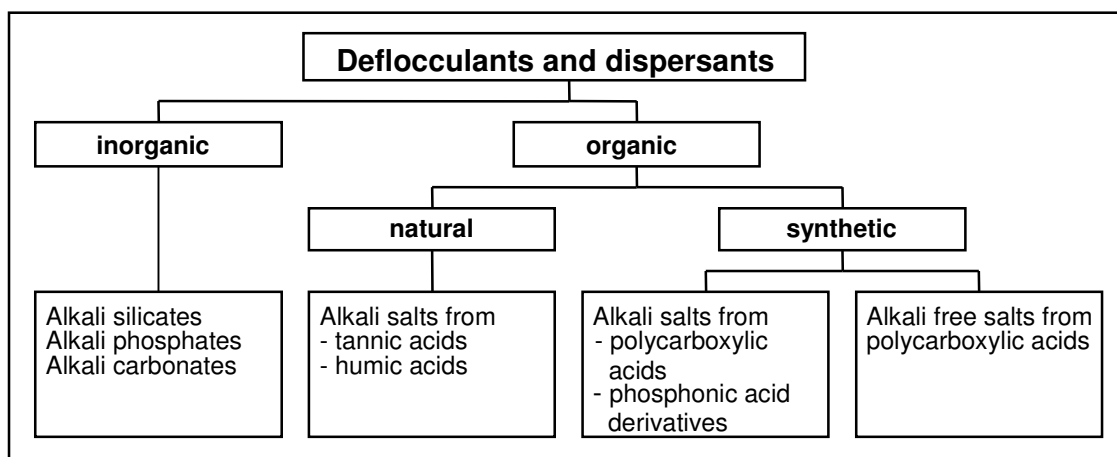


Fig. 12 Overview of the raw materials for deflocculants and dispersants

The following matrix reveals the mechanism of action of the deflocculating effect of the individual raw material types.

	Cation exchange	Steric repulsion	Complexing
Phosphates	●		●
Phosphonates			●
Silicates	●		
Huminates	●		●
Polycarboxylic acids		●	●
Polycarboxylic acid salts	●	●	●

#### 4. Further parameters influencing the water-solids-deflocculant-system

##### 4.1. Solids content of the slip and content of deflocculant

The mutual influence of the electrical attraction potentials of neighbouring particles must be taken into account, particularly at high solids concentrations. Unsuitable deflocculant content can lead to superimposition of the zeta potentials, thus preventing maximum repulsion of neighbouring particles. The consequence can be undesired agglomeration. Figures 13 and 14 clarify these correlations. The red lines illustrate the zeta potential.

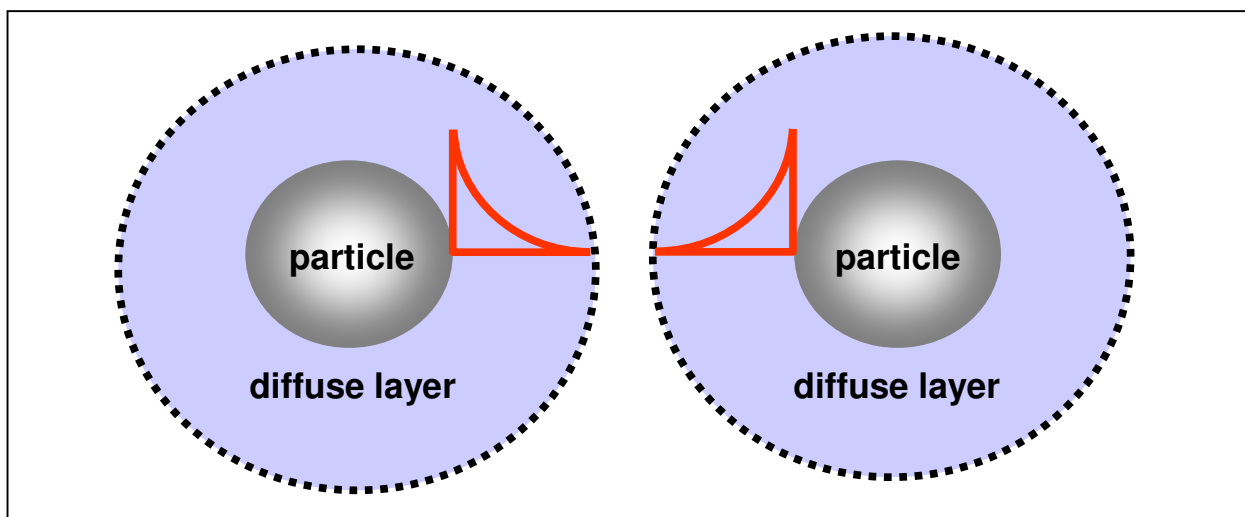
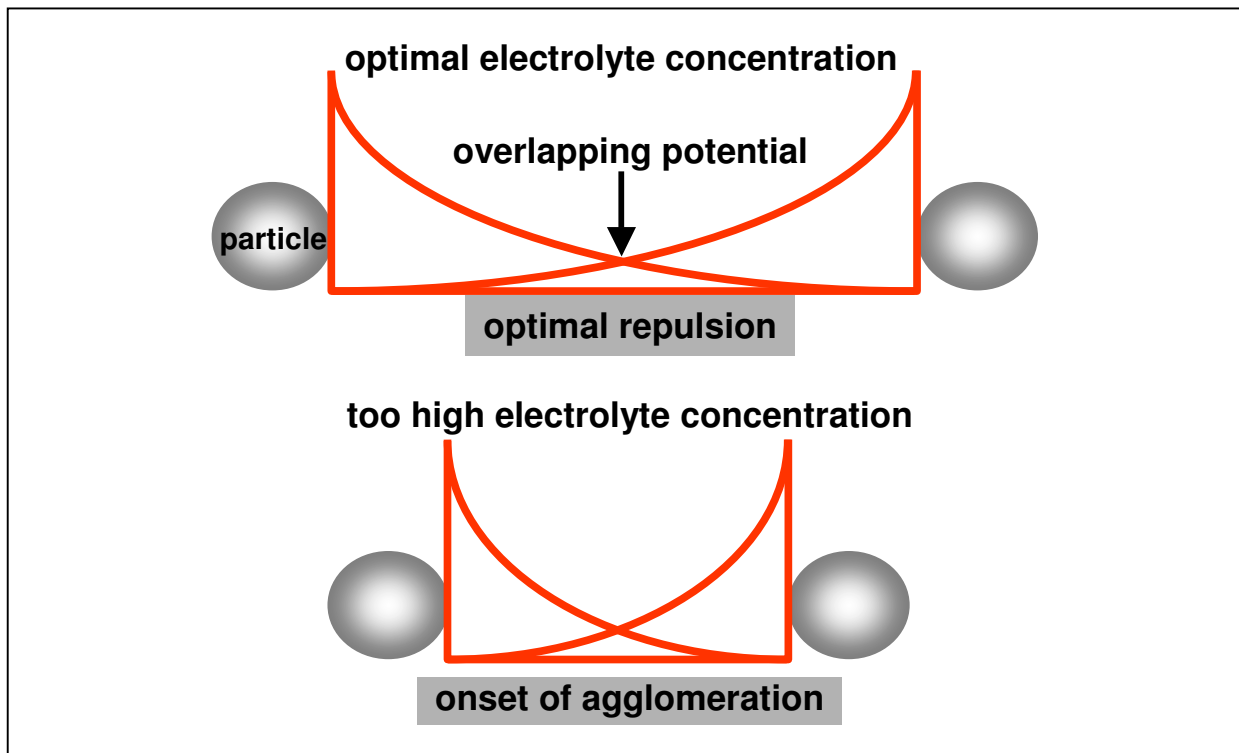


Fig. 13 Raw material particles with diffuse layers without mutual interaction

Two raw material particles with a diffuse layer which do not mutually influence each other are represented in Figure 13. On account of a low density, the distance between them is so large that the zeta potentials do not overlap.

If the density is greater, there is superimposition of the zeta potentials of neighbouring raw material particles. Figure 14 illustrates schematically the superimpositions of zeta potentials with optimal and with too high electrolyte concentration.



**Fig.14** Overlap potentials of neighbouring raw material particles

At optimum electrolyte concentration, the zeta potentials of the neighbouring particles set up an ideal equilibrium between attractive and repulsive forces. This leads to optimum repulsion between the particles.

If more than the optimal quantity of deflocculant is added, the diffuse layer becomes thinner with increasing electrolyte concentration. At too high electrolyte concentrations the attractive forces predominate once again, the tendency to agglomerate increases because the diffuse layers are too thin.

On account of the smaller distances between raw material particles, the agglomeration tendency of slips, which have a too high content of deflocculant, increases with increasing density.

#### 4.2. Temperature of the slip

High slip temperatures lead to increased water evaporation. The loss of water necessarily affects the density. The equilibrium between attractive and repulsive forces in the water-solids-deflocculant-system is changed and, hence, the viscosity of the slip as well.

#### 4.3. Slip ageing

With silicate ceramic bodies, an extended standing time leads to a better breakdown of the clay mineral particles. An increase in the viscosity would be the result.

Changes can also take place in the water-solids-deflocculant-system during a prolonged standing time. Since more time is available for cation exchange it is possible that the viscosity may drop.

The effects can interfere with each other so that it is frequently not possible to make a clear assessment.

#### 5. Summary

The rheology of fluidized aqueous ceramic slips is determined by the interaction between water, solids and deflocculant. The water is characterized by the dissolved salts it contains, which determine its pH and its degree of hardness. The interaction of the water with the solids is influenced by the chemical, mineralogical and morphological parameters of the latter.

The water-solids system is characterized by the agglomeration tendency, on account of electrostatic attraction forces between the raw material particles. The agglomeration brings about high viscosities and the flow properties of the slip are not optimal. Hence, the aim of deflocculation is to break up existing agglomerates and to inhibit agglomeration directly and in the long term. This is brought about by deliberately creating repulsive forces between the raw material particles.

Here there are basically three mechanisms of action:

- cation exchange and, thus, an effect on the thickness of the electrical double layer of the raw material particles
- steric repulsion by the introduction of functional groups, which act as spacers between the raw material particles
- binding of interfering cations by complexing

Since the strength of the attractive forces is a function of the parameters influencing the water and the solids, differing quantities and differing mechanisms of action of deflocculant are necessary. It is of decisive importance that each individual component of a system and the effects of their interactions be taken into account. This is a necessary condition for an optimal result which not only applies when adjusting the desired rheological properties but also when looking for faults in an otherwise functioning system.

The complicated and very different interactions described above for the deflocculation of ceramic raw materials, require extensive laboratory tests. For many years, Zschimmer & Schwarz has carried out developments with very different ceramic raw materials and obtained considerable experience in close co-operation with the customers and is, thus, able to offer a wide range of effective deflocculants and dispersants.