

# ELECTROLYTE USED IN COMPLEX EROSION PROCESS - KAOLIN

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**Abstract:** *The kaolin is part of the clayey suspension, which may be used as working environments through complex electrical erosion. Within these suspensions forming the passive film is explained through electrophoresis when a process of migration of the particles charged electrically toward one of the electrodes under the action of the electrical field takes place. Forming the passive film takes place because of the colloidal micelles resulted through the dissociation of the kaolin, which due to their negative charge, they are fixed on the anode, through forces of absorption. Because these forces are weak, the film has a low adherence and it does not protect correspondingly the piece favouring the electrical discharge in more than one point.*

**Keywords:** complex erosion, kaolin, anode, pasive film, ion.

## 1. THE ROLE OF KAOLIN IN COMPLEX EROSION PROCESSING

Kaolin is part of clay slurries that can be used as working environments for complex erosion processing. In these slurries the formation of the passive film on the surface of the anode is explained by electrophoresis when a process of migrating electrically charged particles towards one of the electrodes under the action of the electric field.

The main structural component of kaolin is kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), which is negatively charged in relation to water, so that the colloidal particles in suspension will migrate to the anode.

The passive film (PF) formed on the OP surface has poor mechanical and electrical properties, which is why large voltages and currents ( $I = 100\text{-}250\text{A}$ ,  $U = 28\text{-}30\text{V}$ ) are required for complex electrical erosion.

The formation of the passive film is due to colloidal micelles resulting from the dissociation of kaolin, which due to their negative loads are fixed on the anode by adsorption forces. As these forces are weak, the film has a low adhesion, does not protect the piece properly favoring electrical discharge in multiple points.

## 2. GENERAL CONSIDERATIONS REGARDING KAOLIN

### 2.1 Hydration of kaolin particles

The water adsorbed on the surface of the kaolin particles forms coatings whose thickness depends on a number of factors: the nature of the crystalline network, the nature and concentration of the adsorbed or water ions.

The aqueous coatings consist of:

- a) water directly adsorbed on the surface of the particles through hydrogen bonds;
- b) solvation water represented by water molecules bound through solvation to the adsorbed ions on the surface of the particles.

The hydrogen junction between clay and water is accomplished by water hydrogen and the oxygen ion on the tetrahedral ( $\text{SiO}_4$ )<sup>-4</sup> layer of the crystalline network. The hydrogen bond appears in the compounds of highly strong electronegative  $\text{H}_2$  elements.

Due to the appearance of hydrogen bonds around the kaolin particles, a first layer of water dipoles hydrogen directed towards the surface of the particle is formed; there are a number of other layers whose degree of arranging and of the intensity of the bond decreases as the distance from the surface of the particle increases.

Adsorption being a superficial phenomenon, the amount of water adsorbed by the kaolin particle is proportional to its degree of dispersion and its specific surface area, respectively. For the kaolinite layers, the thickness of the aqueous coatings ranges from 5 nm to 60 nm.

Water in coatings has a range of properties that distinguish it from the normal one. The water density is between  $1.2 \div 2.4 \cdot 10^3 \text{ kg/m}^3$ .

The adsorbed water does not have the capacity to dissolve, such a coating behaving in a manner close to that of a solid elastic body. The structure of the adsorbed water is explained either by the "solid" or the "two-dimensional" model. According to the "solid" model, the water molecules are not rigidly fixed in an ordered network, however, the degree of ordering is still higher than that of the liquid water. The "two-dimensional" model provides bonds between adsorbed water molecules in a preferential plan with the surface of the adsorbed water in smaller numbers than that of free water, but much more powerful.

The aqueous coats adsorbed by kaolin particles, along with water bonded through solvation, influence the interactions between the particles.

The colloidal nature of kaolin slurries is based on phenomena such as adsorption capacity, the formation of the double dielectric layer and that of the aqueous coating around the particles.

The structure, interaction forces between the particles and therefore the properties of the kaolin slurries depend on: a) the mineralogical composition, the degree of dispersion of the suspension; b) the concentration of the suspension; (c) the nature and concentration of ions and surfactants adsorbed on the surface of particles dissolved in water. By acting on these factors, the suspension properties may change.

## 2.2 Electric charge of kaolin particles

The occurrence of electrical charges at the surface of the kaolin particles can be explained as follows: the hypothesis of the broken bonds: a mineral particle can be considered as a segment of the crystalline network in which the sides parallel to the cleavage plan have a larger weight than the lateral sides, which, in fact, represent the breaking sides of the grid.

As a result of the breaking of the network elements in these sides, unsaturated ions,  $\text{HO}^-$  and  $\text{O}^{2-}$  anions and  $\text{Al}^{+3}$  and  $\text{Si}^{+4}$  cations appear.

The fraction of the elementary electrical charge that is ascribed to each broken bond is given by the ratio between the electrical charge of the respective ion to the coordination number.

Thus, the Al-OH bond from kaolin corresponds to the  $\text{OH}^-$  load of  $-1/2$  because at the 6 of  $\text{Al}^{+3}$  coordinate, a bond is ascribed  $1/2$  of the positive charge which with  $\text{HO}^-$  gives an excess load  $-1/2$ . In this way, the two broken bonds of  $\text{Al}^{+3}$  correspond to  $+1/2$ , the  $\text{O}^{2-}$  ion from the Al-O-Si- $1/2$  bond and the  $\text{Si}^{+4}$  ion  $+1$  load.

Clay mineral particles suspended in pure water retain  $\text{HO}^-$  ions in the positive sectors and  $\text{H}^+$  ions in the negative ones.

In basic aqueous mediums ( $\text{pH} > 8$ ) negative charges on the lateral surfaces can be kept as such, since the alkaline cations adsorbed from the solution dissociate more or less intensively leaving excess negative loads on the surfaces. Positive areas of rupture are adsorbed by  $\text{HO}^-$  ions. Broken bonds are the main cause of the appearance of superficial

electrical charge of kaolinite particles.

According to more recent views, the electrical charge of the kaolinitian mineral particles in the aqueous medium would not be located mainly in the rupture areas or would not occur by adsorption of  $\text{HO}^-$  ions on the neutral surface of the particles but on the base surfaces due to the isomorphous substitution from the network. The fact that the substitution in the kaolinite network of higher valence cation through others with lower valence could not be ascertained by analysis is explained by the fact that due to the low adsorption capacity of kaolinite it is sufficient that out of 200 atoms in the network only one is substituted.

Another explanation for the occurrence of the negative charge of kaolinite particles is the presence at their surface of small quantities of minerals for which the substitution is typical and which, with a negative load, they also confers it to the surfaces they adhere to.

### 2.3. Electrokinetic phenomena, flocculation and peptization of kaolin suspensions

The negatively charged kaolin particle attracts from the environment where it lies a number of cations required by the neutralization of its load.

The anions on the surface of the particle together with the compensating cations form the double electric layer Gouy-Freundlich-Charpman, which in a recent form, according to Stern has the following form (Figure 1):

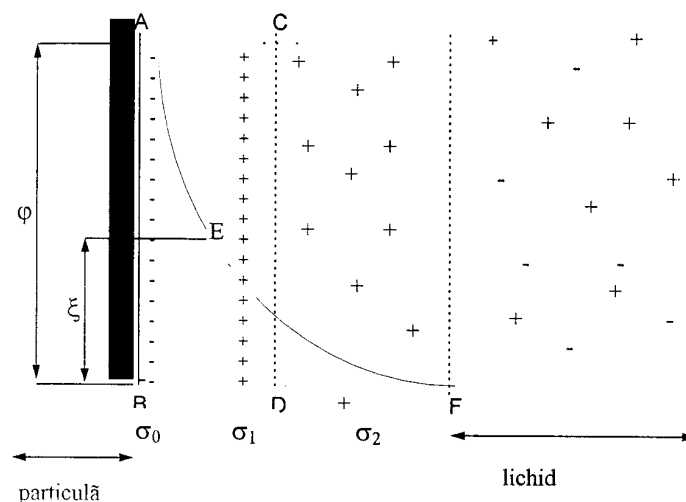


Fig. 1 Double Gouy-Charpman electric layer

Kaolin particles with negative electric charge form Helmholtz's bottom layer that can be assimilated to the internal casing of a condenser with the  $\sigma_0$  density of the loads.

The cations in the liquid phase attracted by the particle form the external casing of the condenser. The first cation layers are very close to the surface of the particle to which they are strongly attracted forming the adsorbed layer or the fixed layer (the Stern layer) with the density of the  $\sigma_1$  loads. Some of the cations that compensate for the charge of the particle as a result of thermal agitation lie in a second layer, their number asymptotically decreasing to that of the remainder of the liquid while departing from the surface of the particle. This is the diffuse layer (Gouy) with the load density  $\sigma_2$ . The system is electroneutral on the whole:

$$\sigma_0 = \sigma_1 + \sigma_2.$$

Cations in the adsorbed and diffused layer form the adsorbed complex. The colloidal

particle together with the adsorbed complex forms the clay micella.

Between the electrically charged surface of the particle and the liquid there is a certain difference of potential. The cations in the adsorbed layer partially neutralize the negative charge of the particle causing the decrease of the difference of potential difference. At the CD limit there is a difference of potential lower than the total one ( $\varphi$ ) called electro-kinetic potential or potential  $\xi$ .

The electro-kinetic potential is the factor that largely determines the nature and intensity of the interaction forces between the particles. The electro-kinetic potential  $\xi$  can serve as a criterion for assessing the interaction between the liquid and the particle as well as between the particles.

In order to monitor the influence of electrolyte additions, the following relationship is used to calculate the electro-kinetic potential:

$$\xi = \frac{4\pi ned}{\varepsilon} \quad (1)$$

where:

n is the number of negative charges on the surface of the particle or the compensating cations;

e - elementary electrical charge;

d - the thickness of the double electric layer;

$\varepsilon$  - dielectric constant of the liquid.

Two constant forces of action act on the clay particles in an aqueous suspension. On the one hand, they reject each other as a result of their task of the same sign. The rejection forces

between them begin to work only when their electrical layers intertwine

In addition to the potential barrier that arises due to the electrostatic discharge forces, there is also a barrier that opposes the approaching of the particles. This is the mechanical barrier of potential due to the water film around the kaolin particle, consisting of the hydration layers of the contraion and the water molecules adsorbed directly at the surface of the particles. The mechanical barrier of potential consists of elastic resistance due to the viscosity of the aqueous film which opposes the approaching of the particles.

A contrary attraction is exerted by the Van der Waals attraction forces that occur when particles, as a result of thermal agitation, are sufficiently close to one another. These forces cause a sensitive attraction between particles at small distances

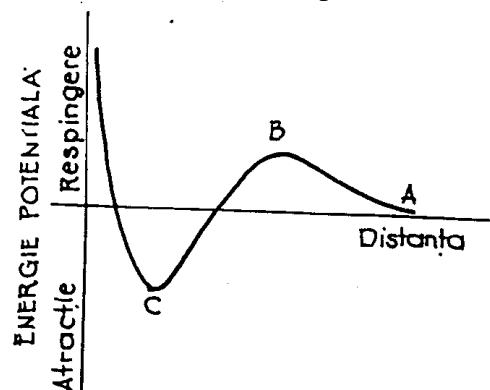


Fig. 2 The variation of potential energy  $E_p$  with distance between the particles

When the particles can get close enough to enter the range of Van der Waals forces, they merge into large aggregates. There is a tendency to flocculate, the suspension becomes unstable. If the rejection forces act too distantly for the forces of attraction to become prevailing, the particles reject each other with the peptisation that ensures the stability of the suspension. Distances to which particles can approach determine the sense of the resultant of the forces acting on them (Figure 2).

Any factor that can influence the value of the potential  $\xi$  also influences the stability of the system. In this respect, the modification of the ion *cortex*, of the electrical charge of the particle or the dielectric constant of the liquid, factors that determine the value of the electrokinetic potential, is likely to alter the stability of the suspension.

### 3. CONCLUSIONS

Due to the high temperatures developed during the processing in the working space, kaolinite undergoes structural changes of particular importance.

Through differential thermal analysis (DTA), Mateev and Grigoriev have identified a series of compounds whose negative electric charge causes them to migrate to the positive pole of the current source.

By dissociating kaolin into water, occurs the hydration of the kaolin particles and the adsorption of water through hydrogen bonds forming aqueous coatings around the particles. At the OP surface, impulse electrical discharge favors very high temperatures so that a dehydration process of colloidal micelles takes place in the space around the anode leaving structural components of kaolin, whose elementary component is  $[\text{SiO}_4]^{-4}$

Colloidal kaolin micelles can be represented by the following structure:  $[\text{mNnK}^{+(n-x)}\text{A}^-]^{+x}\text{A}^-$ .

where:

m is the number of kaolin particles;

N - nucleus of the micelle formed by a large number of kaolin particles loaded with negative charge;

$n\text{K}^+$  - the number of positive ions giving the electrical charge of the particle, which together with a small number of counterions (n-x) form the adsorption layer;

$x\text{A}^-$  - the number of counterions in the diffuse layer.

The adsorption layers and the diffuse layer in the case of colloidal micelles of kaolin are made up of water molecules. In kaolin-based aqueous suspensions, electrostatic discharge forces (being loaded with electrical charges of the same sign) occur as well as a mechanical rejection due to the resilient resistance of the film that opposes the closer movement of the particles.

By dehydration, the colloidal micelles lose the adsorption layer and the diffuse layer, appearing Van der Waals attraction forces, resulting in the formation of large aggregates, which ultimately generate the passive film.

The use of kaolin in complex electric erosion processing has the following advantages:

- increases the productivity of the process by increasing electrical current and voltage;
- The sampling through thermal impulses action is considerably higher than in the case of using soluble glass for the same electrical regime. This phenomenon occurs due to the mechanical passivation with a relatively poor film, which is why there is a tendency to establish discharge in the form of local springs, especially in areas where the access of the working fluid is difficult;

- no harmful aerosols are released;
- no adherent crusts are formed on the surface of the machine.

Due to the disadvantages of kaolin, its use in processing through complex electric erosion is limited:

- machining inaccuracies, side wear of the tool due to the low mechanical and electrical resistance of the film;
- increased OT wear, requiring high peripheral speeds to reduce wear;
- the piece, due to leakage currents, heats up more than when using soluble glass;
- instability of the colloidal systems results in the deposition of kaolin (in the absence of efficient stirring), with clogging of the equipment.

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