Rudarsko-geološko-naftni zbornik	Vol. 4	str. 147–151	Zagreb, 1992.

UDC 537.39

Stručni članak

MEASUREMENT AND APPLICATION OF ZETA-POTENTIAL

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Key-words: Electrokinetic phenomena, Zeta-Potential, Methods of measurement.

The electrokinetic or zeta-potential is an important parameter of the electrical double layer and represents a characteristic of electrical properties of solid/liquid and liquid/gaseous interfaces. In the paper electrokinetic phenomena in this contact are described as well as measuring methods. Changes of the values of zeta-potential depending on some properties of solid/liquid interface are being considered.

Ključne riječi: Elektrokinetičke pojave, Zeta-potencijal, Metode mjerenja.

Elektrokinetički ili zeta-potencijal važan je parametar dvojnog električnog sloja i predstavlja jednoznačnu karakteristiku električnih svojstava na kontaktu faza čvrsto-tekuće i tekuće-plinovito. U radu su opisane elektrokinetičke pojave koje pri tom kontaktu nastaju, kao i metode mjerenja potencijala. Prikazane su promjene vrijednosti zeta-potencijala u ovisnosti o nekim svojstvima čvrste i tekuće faze.

Introduction

In flotation (today the prevailing method in mineral dressing) as well as in solid/liquid separation the surface properties of the minerals, i. e. the specific surface and surface charge, are of essential importance.

In the mineral-water interface electrical forces are also acting. The ionized solid particle is surrounded by liquid ions charged oppositely to the surface particle. During the movement of the solid particle through the liquid a liquid layer surrounding the particle will move together with it. Thus, ionized particle will carry a thin liquid shell making with it an integral whole. The potential difference between the external surface of that shell and the liquid as a whole is called electrokinetic potential or zeta-potential.

The zeta-potential is used in colloid chemistry for observing the behaviour of dispersive systems in liquids. Besides, the zeta-potential characterizes the electrical double layer on the solid/liquid interface, a fact very important in flotation and flocculation processes (Ocepek, 1989).

In this paper the zeta-potential measuring methods (electrophoresis, electroosmosis, streaming potential and sedimentation) are described as well as the measuring principles of the corresponding devices.

Zeta-potentials of a few minerals of characteristic mineral groups are shown on specimens as well as the relation between potential magnitude and suspension stability.

Electrical double layer on the solid/liquid interface

In the contact with a polar medium (water) the majority of mineral particles show a definite surface charge as the consequence of ionization, ionic adsorption and ionic dissolution. This surface charge influences the arrangement of neighbouring ions of the polar medium. Ions of the opposite sign will be attracted to the particle surface and the ions of the equal sign will be repulsed from the surface. By the added influence of mixing as a consequence of thermic movements and the influence of Brown's movement, an electrical double layer is formed (Shaw, 1970).

This double layer consists of charged surface and a neutralized surplus of opposite-and equally-charged ions diffusely spreading through polar medium. The double layer is characterized by the ion arrangement and the magnitude of electrical potential in the vicinity of the charged particle surface. The existence of the electrical double layer is in close connection with the electrostatic interaction between the particles of suspension and, consequently, with the suspension stability.

The electrical double layer consists of two parts, i.e.: an inner part which includes adsorbed ions and an external or diffuse part in which the ions are arranged under the influence of electrical forces and thermal movements.

Gouy and Chapman proposed a model of the diffuse part of the double layer which assumes the following suppositions:

a) the surface is plane, extending to infinity and uniformly charged;
b) ions in diffuse part bear a unit charge;
c) the polar medium effects the double layer only through its dielectric constant which is unchanged in the whole diffuse part of the layer;
d) the polar medium has the characteristics of a symmetrical electrolite.

Thus, this model shows the relation between the charge, potential and electrolite concentration, neglecting the ion size.

The magnitude of surface charge following this model (Svarovsky, 1977) is given by the equation:

$$\sigma = \left(\frac{\varepsilon\pi kT}{2}\right)^{1/2}\left[\exp\left(\frac{\nu e\Psi_o}{2kT}\right) - \exp\left(-\frac{\nu e\Psi_o}{2kT}\right)\right]$$

where are:
σ – density of the surface charge,
ε – dielectric constant,
k – Boltzman constant,
T – absolute temperature,
e – charge of an electron,
ψ_o – particle potential,
ν – ion valence of opposite charge.

Stern noticed the drawback of neglecting the ion size and therefore proposed a model which starts from the following assumptions:

a) ions have a finite size;
b) ions cannot approach the surface at a distance smaller than the magnitude of ionic radius;
c) the possibility of a specific ion adsorption exists.

The ions which under the effects of electrostatic and/or van der Waals forces adsorb on the particle surfaces, overcoming the effect of thermal movements, are colled specifically adsorbed ions (Shaw, 1970). The centres of these ions are localized inside the Stern plane, that is between the particle surface and the Stern plane (Fig. 1). The ions with centres on the opposite side of the Stern plane form the diffuse part of the electrical double layer (Gouy-Chapman model).

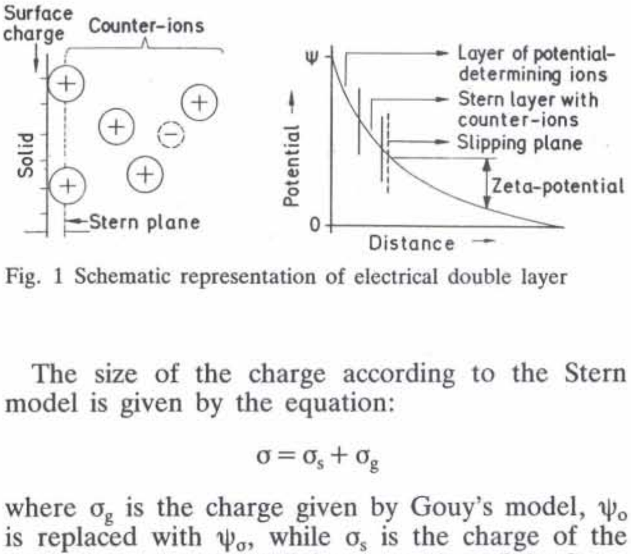

Fig. 1 Schematic representation of electrical double layer

The size of the charge according to the Stern model is given by the equation:

$$\sigma = \sigma_s + \sigma_g$$

where σ_g is the charge given by Gouy's model, ψ_o is replaced with ψ_σ, while σ_s is the charge of the Stern layer. So, the definite expression of the Stern model is written as follows (Svarovsky, 1977):

$$\sigma = n\,\sigma_m\left[n + A\exp\left(-\frac{\nu e\Psi_\delta}{kT} - \Phi\right)\right]^{-1} + \\ + \left(\frac{\varepsilon nkT}{2\pi}\right)^{1/2}\left[\exp\left(\frac{\nu e\Psi_\delta}{2kT}\right) - \exp\left(-\frac{\nu e\Psi_\delta}{2kT}\right)\right]$$

where are:
n – ion concentration,
σ_m – charge density of monolayer of the opposite charged ions,
A – frequency factor,
Φ – van der Waals energy.

The potential on the Stern plane which divides the immovable part of the layer from its diffuse part is called zeta-potential. This potential is a parameter representing electrical properties of an interface.

Zeta-potential and possibilities of its measurement

The explanation of the phenomena connected with the surface charge of a solid phase in contact with a liquid one was made possible by the electrical double layer theory. According to this theory the electrokinetic or zeta-potential is a measurable property of an electrized interface.

If an electrized interface between two phases is under the influence of an external electrical field acting parallel with the interface surface, there arises a relative movement of one phase towards the other. The potential of the sliding plane, which can be experimentaly measured, is the electrokinetic or zeta-potential (Adamson, 1967).

From the above it is clear that the zeta-potential is changing according to the changes in the solution, what means that by zeta-potential measurements it is possible to follow the changes which take place in the solution. Therefore, the measurement of the zeta-potential is an important controlling proceeding in many technical processes.

For zeta-potential measuring electrophoresis is mostly used because the measurements can be carried out relatively simply and quickly, as there are available various measuring devices zetameters, on the market. A limitation of the method presents the particle size of the measured sample of approximately 10 nm . . . 10 μm. Electrophoresis appears when a fine (e. g., colloidal) dispersion of some dielectric matter in the electrolitic solution is exposed to the effect of an electrical field. Single dispersed particles are electrically charged according to the dispersion medium and an electrical double layer is formed around each of them. If the liquid phase as a whole is prevented to flow in one direction, only charged particles will be kept in motion in the electrical field, and they will travel, depending on their charge, towards the catode or anode.

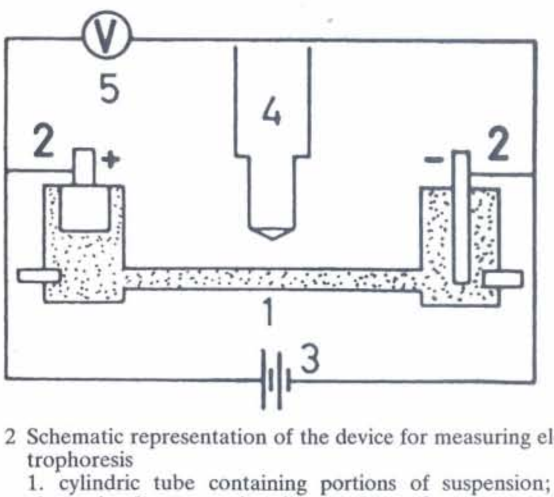

Fig. 2 Schematic representation of the device for measuring electrophoresis
1. cylindric tube containing portions of suspension; 2. electrodes for generating direct voltage: 3. power source; 4. microscope for determing particles mobility speed; 5. measuring insturment.

Electroosmosis can be taken as a complement to electrophoresis. Electroosmosis is the measurement of the flow of a liquid phase through a porous membrane in a known electrical field, with constant temperature. The speed of electroosmotic flow is proportional to the strength by which an external electrical field acts on the charge of liquid phase.

Streaming potential is a phenomenon opposite to electroosmosis. During the passing of the liquid phase through an electrized membrane due to the potential difference of the two electrodes, electroosmosis causes a certain difference of pressures, what again causes a raising of the liquid level. Opposite to this electroosmotic effect, by means of applying pressures in the same system and by forcing the solution through the membrane, a certain potential difference, called the flow potential, can be provoked. It is just proportional to the difference between pressures and the flow speed of the electrolite solution through the membrane pores. The flow potential as well as electroosmosis are phenomena depending on the colloidal membrane and its electrization.

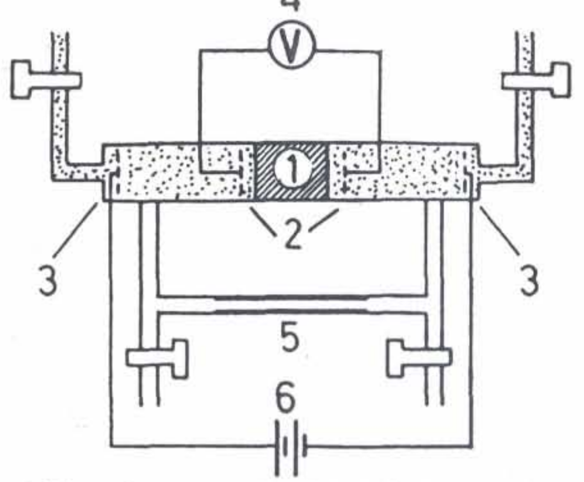

Fig. 3 Schematic representation of the device for measuring electroosmosis
1. porous mass through which solution flows (membrane); 2. measuring electrodes; 3. operating electrodes; 4. measuring instrument; 5. parallel capillary; 6. power source

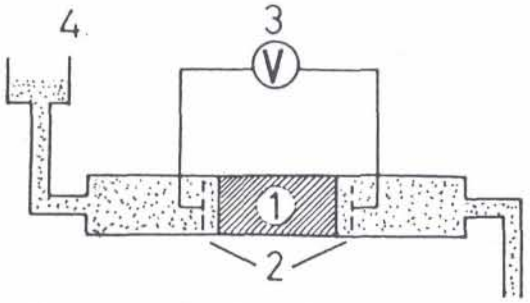

Fig. 4 Schematic representation of the device for measuring straming potential
1. porous mass through which solution flows (membrane); 2. measuring electrodes; 3. measuring instrument; 4. provoking and measuring pressure

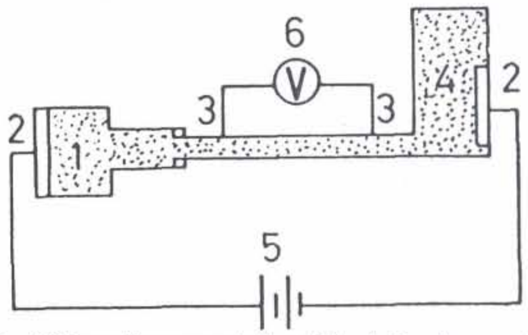

Fig. 5 Schematic representation of the device ofr measuring sedimentation potential
1. container-collector with emptying possibilty for the particles moving towards the electrode; 2. operating electrodes; 3. measuring electrodes; 4. suspension container; 5. power source; 6. measuring instrument

The phenomenon opposite to the electrophoresis is the sedimentation potential. It realizes during the movements of electrized particles in gravitational or sedimentation fields in centrifuges. It is rarely used in the study of electrokinetic phenomena because it is very difficult to be measured.

The importance of zeta-potential in flotation and flocculation

In the flotation process three phases are present: solid, liquid and gaseous. By their interaction it comes to oxidation, hydratation and hydrolysis; that causes lesser or bigger changes in the properties of the mineral surface. Here, two factors are important (Fuerstenau, 1982):

- interaction of water molecules with mineral surface, either in liquid or gaseous surroundings;
- electrical double layer in the solid/liquid interface.

Oriented water layers in mineral surface have a significant effect on wetting the solids, as well as on the nature of adsorption in an interface. On the other hand, electrical double layer can control the processes of flotation in many ways (Fuerstenau, 1982); the following must be mentioned:

- the symbol and size of the surface charge controls the physical adsorption of the flotation reagents;
- a high surface charge can inhibit the chemical adsorption of the collectors;
- the flocculation and dispersion of mineral suspensions is controlled by the electrical double layer;
- slime coatings are determined by electrical double layer interaction;
- the double layer on air bubbles has a significant effect on naturally floating mineral systems;
- flotation kinetics relate directly to the effect of double layers on the kinetics of film thinning.

To be able to separate by means of flotation from some paragenesis only a certain mineral, it is indispensable to know the following about the present minerals (Ney, 1973):

- the sort and compostition (main parts, at least);
- solubility and, if possible, the speed of solubility in clear water, in acids and bases;
- zeta-potential depending on pH values.

On the basis of mineral properties which are manifested during flotation, i. e. which influence their floatability minerals may be divided in a few groups (Ney, 1973):

Group 1: Naturally hydrophobic minerals;
Group 2: Minerals floating with sulfhydrilic collectors;
Group 3: Minerals soluble in acids or sensitive to acids;
Group 4: Oxide and silicate mixtures generally insensitive to acids;
Group 5: Silicates which form monomineral rocks.

Zeta-potentials of some characteristic minerals of the mentioned groups are presented in Fig. 6.

The curve »a« shows the zeta-potential of talc (Group 1) depending on pH values. The zeta-potential depends on the interaction between water ions and the hydrophobic clevage plane but on the hydrophylic side planes of the talc leaves.

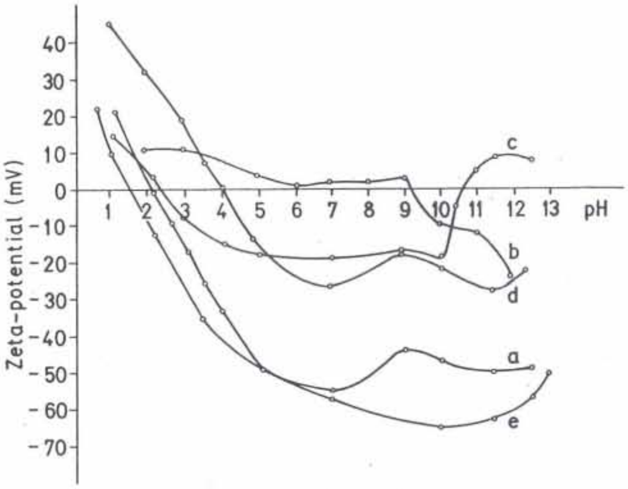

Fig. 6 Depedence of zeta-potential on pH values

The curve »b« shows the zeta-potential of galenite (Group 2) depending on pH values. Electronic holes should prevail on the galenite planes in the range from pH 2 to pH 9, as the zeta-potential is positive in this region. To this groupe belong mineral raw materials which are very suitable subordinate to flotation because they exhibit marked hydrophobia.

The curve »c« shows the zeta-potential of gypsum (Group 3) depending on pH values. A number of mineral raw materials from this group float only in acidd or very acid pH regions though the usage of acids may even have some negative consequences. Gypsum floats in a wide range of pH, both with anion and kation collectors.

The curve »d« shows the zeta-potential of magnetite (Group 4) depending on pH values. For all mineral raw materials of this group the zeta-potential is postitive in more or less acid media, and it is negative in poor acid or alcalic medium. Minerals of high density belong to this group, what influences their floatabiliy.

The curve »e« shows the zeta-potential of the pure quartz (Group 5) depending on pH values. Quartz can be floated with kationic collectors in the whole pH region. Mineral raw materials which have extremely unsuitable conditions for separation of minerals belong to this group.

In the flocculation process the suspension stability of finely ground minerals has an important role. Under stability the resistance of mineral suspension to the change of its state is understood. Suspension stability can be explained by the changing action of attracting forces on one side and repelling forces on the other, what depends on the particle distance. By addition of the attracting and repelling energies the resulting potential curve can be obtained, with a form that depends on the surface potential value, too. Between the zeta-potential and the surface potential there is an interdependence which is not proportional.

From the size of the zeta-potential no direct conclusions about the suspension stability can be drawn, although from a number of zeta-potential measurements as well as from the other investigations with very different colloides and finely ground minerals and mineral mixtures it could be shown that the following dependences are valid (Riddick, 1967).

Table 1. Change of suspension stability depending on zeta-potential size

Assessment of stability	Zeta-potential (mV)
Maximal agglomeration and precipitation	0 . . . + 3
Region of strong agglomeration and precipitation	+ 5 . . . − 5
Beginning of agglomeration	− 10 . . . − 15
Beginning of peptization (disperging)	− 16 . . . − 30
Medium stability	− 31 . . . − 40
Good stability	− 41 . . . − 60
Very good stability	− 61 . . . − 80
Extremely good stability	− 81 . . . − 100

From Table 1 it can be seen that stability is at the lowest in the vicinity of a point where the value of zeta-potential is approximately equal to zero. Therefore, if the suspension is to be destabilized, one of the ways is to lower the zeta-potential, i. e. to reduce the electronegativity of a particle. A markedly strong agglomeration is achieved by adding longchained polymers which cause a mechanical linking of single particles, i. e. of smaller flocculi into bigger ones.

In the Fig. 7 the electrokinetic potential of red mud is shown (the insoluble residue after bauxite leaching) with addition of polymers of different molecular mass and ionogenity (Salopek, 1982).

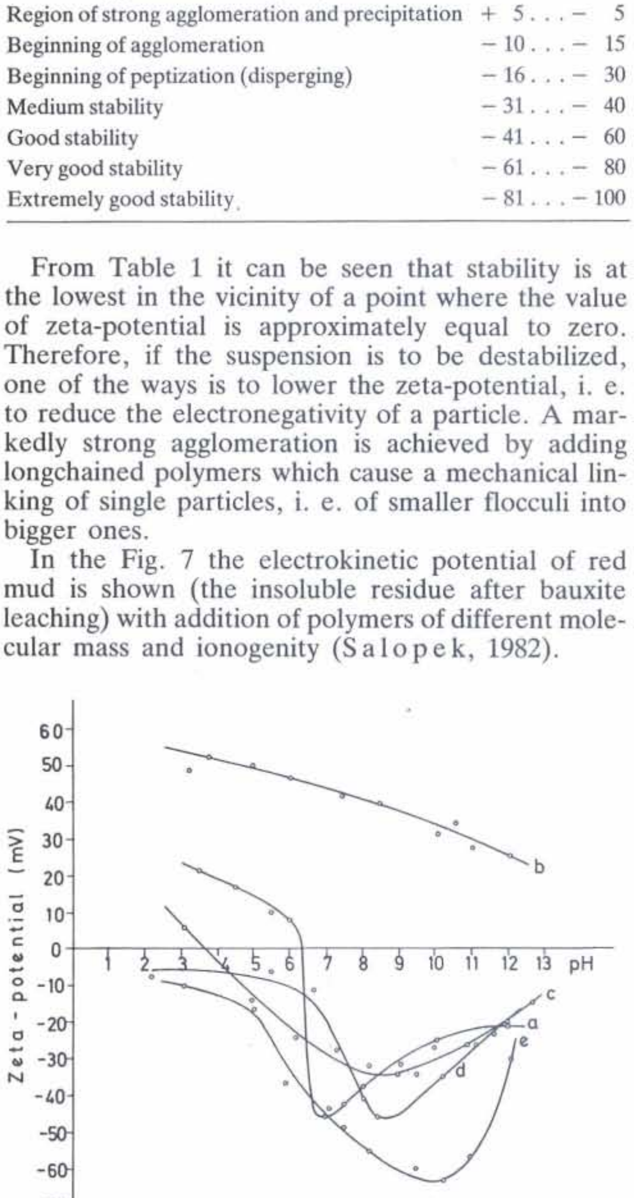

Fig. 7 Zeta-potential of red mud.

The curve »a« shows the zeta-potential of a simple without addition of a flocculant. In acid regions the potential is positive and in alkali regions it is negative. In the isoelectric point at pH 6,3 . . . 7, an abrupt change of concentration of potential determining H^+, i. e. OH^- ions in the electrical double layer takes place. In this narrow pH region the potential abruptly increases from 0 to 45 (mV), approx.

The curve »b« shows the zeta-potential of red mud with an addition of kationic flocculant Praestol 184 K of molecular mass 5×10^5. This flocculant shows a positive zeta-potential which from the value of 55 (mV) in acid regions gradually drops to 25 (mV) in alkali regions. In a sedimentation experiment a very pure overflow has been obtained.

The curves »c«, »d« and »e« show the zeta-potential with an addition of anionic flocculants A-6, Flocgel, Praestol 2450, of the molecular mass $5 \ldots 10 \times 10^6$, $5 \ldots 10 \times 10^5$ and 5×10^5. The zeta-potential is negative during the whole measuring region, with the exception of flocculant A-6 which shows positive values between pH 3 and 4. In the region of pH 8 . . . 10,5 the values of the zeta-potential are in accordance with sedimentation experiments but as well as with the molecular mass of single flocculants. A less zeta-potential and greater molecular mass give more masive flocculi and a purer overflow. The influence of polymer flocculants depend much more on their molecular mass than on ionogenity.

Therefore, a kationic flocculant is not indispensable for the destabilization of an electronegative suspension as well as the anionic flocculant is not indispensable in the case of a highly positive zeta-potential.

Summary

A greater part of investigations of mineral zeta-potentials is based on the presumption of an interacting dependence between the zeta-potential and mineral floatability. The results of such investigations, obtained by eminent scientists, are very different. The reason is that the zeta-potential of any material in water solutions is defined not by one specific process only but it is a consequence of a series of processes, as stated before. Also, during the flotation process there are mainly artificial surfaces which in the sense of energy are always much richer than natural surfaces; further on, all experiments are performed in water or in the air, what causes many changes on the mineral surfaces. Since the mineral surface is not composed homogeneously of particles with an identical charge, it shows a more or less changing activity, what is reflected in the zeta-potential.

In solid/liquid separation, as well as in other processes where flocculation is used, the inclination to stability changes of the suspension cannot be estimated just on the basis of the zeta-potential size, although a certain connection between the stability and the zeta-potential surely exists.

The zeta-potential can help in the choice of flocculants but a definite valuation of its applicability can be given only after sedimentation or other suitable tests.

Received: 8. I. 1992.

Accepted: 9. VI. 1992.

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Mjerenje i primjena zeta-potencijala

B. Salopek, D. Krasić i S. Filipović

Veći dio ispitivanja zeta-potencijala minerala odnosi se na pretpostavku međusobne ovisnosti zeta-potencijala i flotabilnosti. Rezultati ispitivanja ove ovisnosti vrlo su različiti. Uzrok tome je činjenica da zeta-potencijal nekog minerala u vodenoj otopini nije definiran samo jednim specifičnim procesom nego je posljedica niza procesa. Također, u procesu flotiranja uglavnom se radi o umjetnim površinama, koje su u energetskom smislu uvijek bogatije od prirodnih površina, a i svi se pokusi izvode u vodi ili na zraku, što naravno ima za posljedicu promjenu mineralnih površina. Zato što mineralna površina nije sastavljena homogeno od čestica identičnog naboja, ona pokazuje više-manje promjenljivu aktivnost, što se odražava i na zeta-potencijalu.

U postupcima razdvajanja faza čvrsto-tekuće, kao i u ostalim postupcima gdje se koristi flokulacija, ne može se samo na temelju veličine zeta-potencijala procjenjivati sklonost promjene stabilnosti suspenzije, iako nedvojbeno postoji određena veza između stabilnosti i zeta-potencijala. Zeta-potencijal može biti od pomoći pri izboru flokulatora, ali konačna se ocjena njegove podobnosti može donijeti tek nakon provedbe sedimentacijskih ili drugih prikladnih testova.