CHARACTERIZATION OF KAOLIN DISPERSION USING ACOUSTIC AND ELECTROACOUSTIC SPECTROSCOPY

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Dedicated to Prof. Ing. Jaroslav Šesták, DrSc. at the occasion of his 70th birthday

Abstract

The objective of this work is the investigation of the kaolin dispersion by the ultrasonic techniques. In contact with aqueous solution clay minerals show cation - exchange properties and certain degree of dissolution or rather selective leaching of components. The work is divided into two main parts – determination of zeta potential and particle size distribution. The first part is focused on measuring of zeta potential. Effects of concentration of solid, different kind of electrolytes (0.01 M KCl, 0.01 M MgCl$_2$ and 0.01 M CaCl$_2$), pH and temperature of the dispersions are investigated. The isoelectric points (IEP) of kaolin suspension are about pH 4-5. Electrolytes containing monovalent cations such as K$^+$ become zeta potential more negative compared to the values obtained with water. Such behaviour is explained by the exchange of K$^+$ ions with H$^+$ ions in the system. When the electrolyte is formed by divalent cations such as Mg^{2+} or Ca^{2+}, the values of zeta potential become less negative than zeta potential of kaolin in water.

The second part is focused on the determination of particle size distribution with respect to dispersing conditions, such as the optimal dispersing agent (Na$_2$SiO$_3$, (NaPO$_3$)$_6$, Na$_4$P$_2$O$_7$ or Busperse), time and power of ultrasonication and also the tracking of dispersion stability that is expressed by the measuring of particle size distribution during certain time period.

Keywords: kaolin, zeta-potential, isoelectric point, thermal behavior

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1. Introduction

Characterization of particle dispersion is important to optimize and control for example ceramic forming processes, paints, printing inks, dyestuffs etc. [1]. Two very significant characteristics of aqueous dispersions are particle size distribution (PSD) and zeta potential (ξ-potential) which express the charge at the shear plane of the electric double layer (EDL). The thickness of this layer is also a determining factor for the electrostatic repulsion and thus for description of the dispersion stability. High thickness of the double layer occurs when the ionic concentration in the medium is low. By adding an electrolyte, the ionic concentration is raised and thereby the thickness of the double layer is reduced. Flocculation of the system arises when the double layer is so thin that electrostatic repulsion does not suffice to compensate the attractive forces [2].

The effect of the particle charge of clay minerals on the aggregation behaviour, sedimentation or filtration is the main object of the several researches [3-7]. Marek Kosmulski et al. have widely investigated electrokinetic properties of clay minerals and anatase at high ionic strengths [5, 8]. Their results regarding clay minerals measurement indicate that the electrokinetic potential does not cease at high ionic strengths. Potassium and cesium salts induced a shift in the isoelectric points (IEP) of kaolin to high pH [5]. In the case of measuring of anatase they found that an increase in the ionic strength induces a shift in the IEP of anatase to high pH. When the concentration of salt NaI exceeded 0.5 mol dm^{-3} the zeta potential is positive up to pH 11 and probably there is no IEP at all [8]. Close attention also was paid to the study of the ξ-potential of alumina powders [9]. A. López Valdivieso et al. studied among others the effect of temperature and pH on the zeta potential of α- Al$_2$O$_3$. They found that the increasing temperature from 10 to 40°C causes the shift of the pH of the IEP to lower values in consequence of proton desorption from the alumina surface [10].

The objective of this work was the investigation of the concentrated kaolin dispersion by the ultrasonic techniques with DT-1200 instrument. The work is divided into two main parts – determination of zeta potential and particle size distribution. Effects of concentration of solid, temperature and the pH and the different kind of supporting electrolytes on the zeta potential are investigated. The second part is focused on the determination of particle size distribution with respect to dispersing conditions, such as the optimal dispersing tanning agent (Na$_2$SiO$_3$, (NaPO$_3$)$_6$, Na4P$_2$O$_7$ and "Busperse"), time and power of ultrasonication and also the tracking of the dispersion stability that is expressed by the measuring of particle size distribution during certain time period.

2. Experimental

2.1 Sample characterization

Kaolin has well defined chemical formula and crystal structure, but actual samples of kaolin vary in composition. An electron microscope, JOEL JSM 5500 LV, JOEL Inc. USA, was used to characterize the kaolin sample with respect to particles overall appearance. Fig. 1 shows that the shape of

particles is far from spherical. The chemical composition of kaolin sample was determined by EDX using IXRF system and Gresman Sirius 10 detector and is given in Table 1.
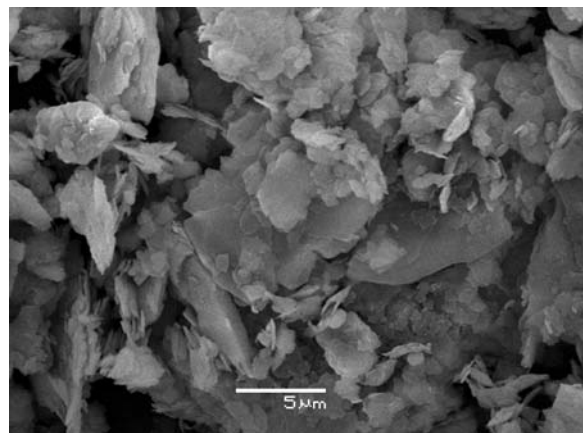

Fig. 1. Shape characterisation of kaolin sample

Table 1. Chemical composition of kaolin

Element	Atomic percentage present [%]
O	65.876
Mg	6.356
Al	12.433
Si	14.886
K	0.7
Fe	0.267

Thermal behaviour of kaolin sample was studied by methods of thermal analysis. Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (NETZSCH, Germany) in the temperature range 30-1150°C at heating rate 10 °C.min^{-1}. The analysis was carried out in a ceramic crucible under air and - Al_2O_3 was used as a reference material.

2.2 Sample preparation

Kaolin samples were treated before using in the experiments as follows: the each slurry containing 1 - 30 wt % of kaolin in distilled water or electrolyte solutions (KCl, $MgCl_2$ or $CaCl_2$) was prepared by mechanically stirring for about 10 min. Then the each slurry was homogenized by ultrasonic processor UP400S (Hielscher Ultrasonics, GmbH, Germany) usage of 100 % amplitude of ultrasonication (400 W) in pulse mode for 10 minutes. After waiting for about 1 minute the electrokinetic properties of the slurries were measured. The pH value of the slurries was adjusted with 2 M HCl and 1 M NaOH.

2.3 Measuring methods

Information about the electrokinetic properties and the PSD of kaolin dispersions were obtained by using electroacoustic spectrometer DT-1200 (Dispersion Technology, USA) instead of laser-based instrument. This method belongs to the category of acoustic and electroacoustic spectroscopy. The advantage of these techniques is the possibility of propagating ultrasound through samples that are not transparent for light and therefore, the ultrasonic techniques offer a unique opportunity to characterize concentrated dispersions. Ultrasonic techniques characterize the sample in two steps. The first step represents the measuring of some macroscopic properties. In the case of acoustic spectroscopy it is measuring the attenuation of ultrasound within a certain frequency range. Electroacoustic spectroscopy provides two implementations depending on driving force. One of theme, Colloid Vibration Current (CVI), is generated by the sound wave as it passes through the dispersion. The second step

involves some theoretical treatment of the measured raw data which purveys the desired information [11].

3. Results

3.1 Thermal behavior of kaolin sample

Thermal decomposition of kaolin sample was followed by methods of thermal analysis. The TG and DTA curves are shown in Fig. 2. The first endothermic effect with minimum at 129°C is connected with loss of moisture. Real thermal decomposition of kaolin sample started around temperature 500°C. The distinct endothermic effect on

925-1050°C corresponds with partial elimination of silica oxide, which stays at amorphous state and with formation of another metastable intermediate product with spinel structure [12]. These processes are recorded on the DTA curve by two effects. The first small endothermic effect has minimum at 929°C and the main exothermic effect is characteristic by maximum at 1049°C. The total decomposition of kaolin sample is finished around the temperature 1200°C by formation of cristobalit. This exothermic effect is not detected at the DTA curve of the Figure 2, because the measurement temperature interval was 30-1150°C. The decomposition of kaolin is also
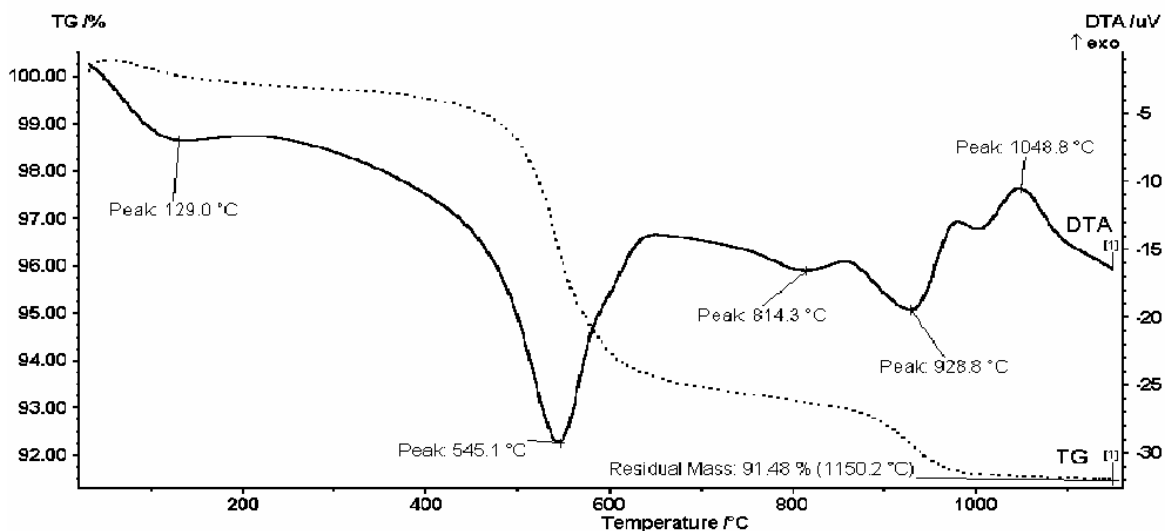

Fig. 2. Thermal decomposition of kaolin sample

the DTA curve with minimum 545°C corresponds to the dehydration of sample. The loss of structural water leads to the formation of metastable product related to kaolinite. Further endothermic effect with minimum at 814°C is the most probably connected with compaction of the metastable product. The temperature region between

detected on the TG curve by mass loss. The total residual mass is 91.48 %.

### 3.2 The effect of solid to liquid concentration on the zeta potential

The concentration of solid in slurry is a major parameter affecting the surface charge

generation. The equipment DT-1200 is primary intended for the measuring of electrokinetic properties of the concentrated systems. Thus, the determination of the most appropriate solid concentration in the slurries was the first goal. The Figure 3 shows the effect of kaolin concentration in distilled water on the value of the ξ-potential of the slurry. The increasing concentration of kaolin from 1 to 7.5 wt % causes significant increasing of absolute value of zeta potential. Concentration 7.5 wt % and higher stabilize the values of the zeta potential of kaolin in distilled water at about -33 mV. Therefore, in the subsequent zeta potential measurements the solid-to-liquid concentration was kept as 10 wt. %.

surface charge of kaolin in aqueous dispersion is negative. The electrical charge at the oxide surface/aqueous phase interface can be described as [6]:

$$-MOH + H^+ \leftrightarrow MOH_2^+ \qquad (1)$$

$$-MOH + OH^- \leftrightarrow -MO^- + H_2O \qquad (2)$$
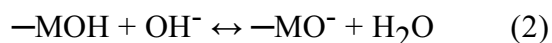
At IEP there is no charge at the surface, that is, the total positive charges are equal to the total negative charges (Eq.3).

$$[MOH_2^+] = [-MO^-] \qquad (3)$$
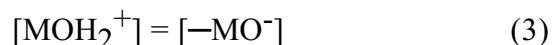
The kaolin dispersion without any chemical additives has pH value around 7.1-8.8, depending on kaolin concentration in distilled water. Results of measurement of the zeta potential as a function of pH of
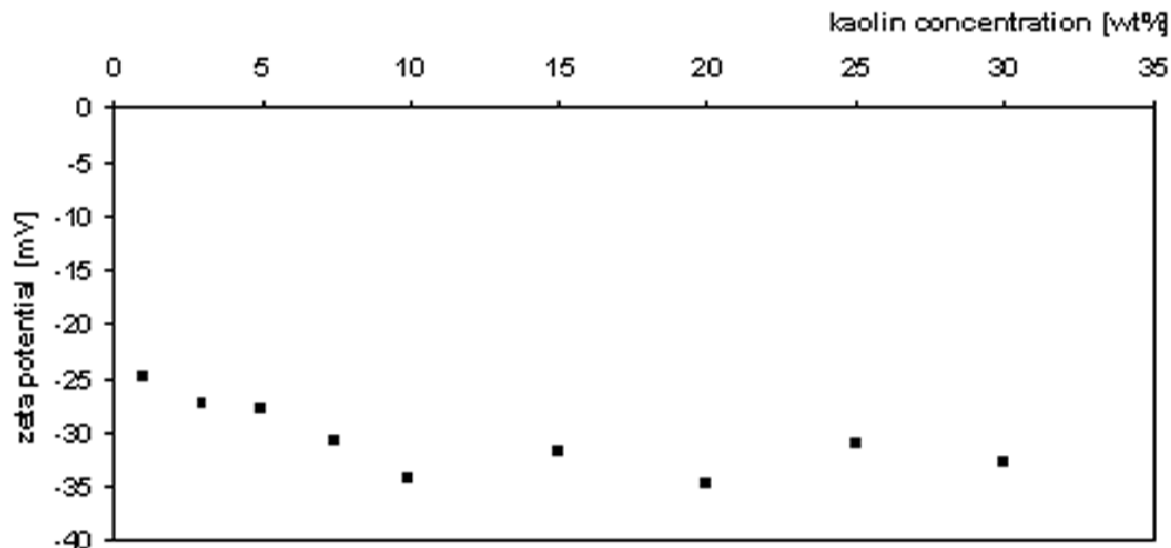

Fig. 3. Effect of kaolin concentration on the values of zeta potential

3.3 The effect of pH and supporting electrolytes on the zeta potential

In contact with aqueous solution clay minerals show cation - exchange properties and certain degree of dissolution or rather selective leaching of components. The

kaolin powders in distilled water and in some supporting electrolyte solutions (0.01 M KCl, 0.01 M $MgCl_2$ and 0.01 M $CaCl_2$) are shown in Fig. 4-7. The IEPs of kaolin dispersions are about pH 3.5-4.5 depending on electrolyte solution.
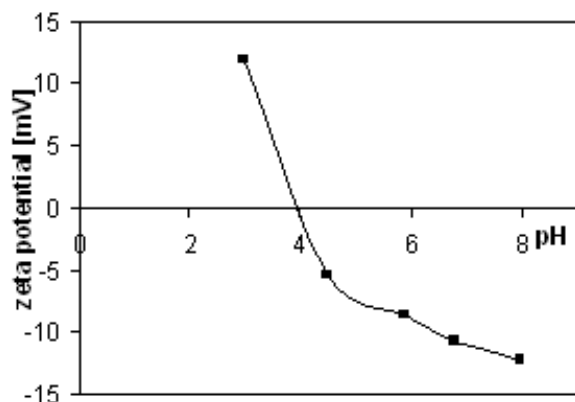
These values are in accord with other

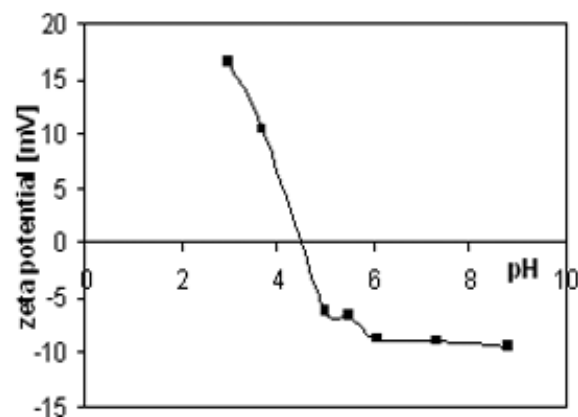*Fig. 4. The zeta potential of kaolin in H_2O as a function of pH*

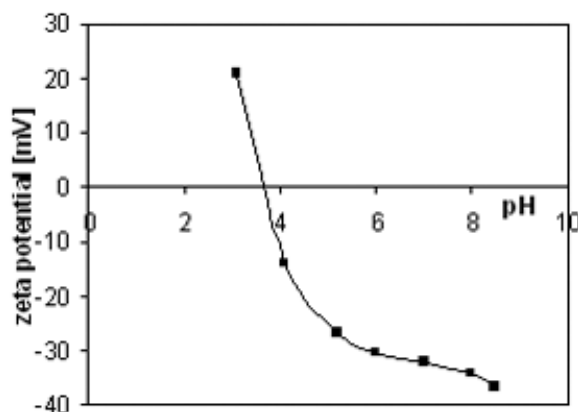*Fig. 5. The zeta potential of kaolin in 0.01M KCl as a function of pH*

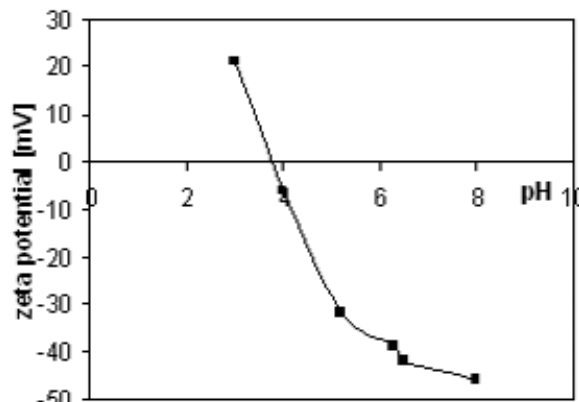*Fig. 6. The zeta potential of kaolin in 0.01M $CaCl_2$ as a function of pH*

Fig. 7. The zeta potential of kaolin in 0.01M $MgCl_2$ as a function of pH

reported values (pH_{IEP} = 2-6) [13]. The variations in the pH_{IEP} of kaolin could be explained by the differences in sample composition, different processing techniques, and so on. The values of pH_{IEP} of the kaolin dispersions increase in the order: H_2O(3.60)–KCl(3.75)– $CaCl_2$(3.98) – $MgCl_2$(4.50). The values of zeta potential of kaolin dispersed in solutions of electrolyte or in water also show two different behaviours in range of pH = 4.5 - 9. Electrolytes containing monovalent cations such as K^+ induce zeta potential more negative compared to the values obtained with water. Such behaviour can be explained by the exchange of K^+ ions with H^+ ions in the system. On the other hand, when the electrolyte is formed by the divalent cations such as Mg^{2+} or Ca^{2+}, the values of zeta potential become less negative than zeta potential of kaolin in water.

3.4 The effect of temperature on the zeta potential

Temperature is the one of the fundamental

quantities applied in almost all models of physical or chemical processes. Temperature affects acid-base equilibrium in solutions, adsorption coefficient and adsorption rate of all participating molecules and ions. It also affects the change of material properties (solid, liquid) and thermal motion of solvent molecules known as Brownian motion. The relation between temperature and zeta potential of α-Al$_2$O$_3$ was described by A.L. Valdivieso. When the temperature increased from 10 to 40°C, the pH of the izoelectric point shifted to lower values in consequence of proton desorption from the alumina surface [10].

The zeta potential of 10 wt. % kaolin slurry in 0.01 M solution of KCl was determined as a function of temperature (Fig. 8). The results show, that the values of zeta potential are slightly sensitive to the temperature variation in two regions. The first thermal zone from 13 to 19°C brings the less negative values of zeta potential (from -37 to -38 mV) and the system is slightly destabilized by coagulation. The system shows the higher stability in the second thermal zone from 20 to 38 °C. The values of

the zeta potential in that zone vary between -43 and -46 mV.

3.5 The measuring of particle size distribution (PSD)

The particle size distribution of the tested kaolin is polydisperse and contains two size maxima peaks. Depending on the way of preparation of the kaolin dispersion, the mean of the first peak (d1) varies among 0.15 and 0.85 µm. The mean of the second peak (d2) varies among 4.4 and 10.6 µm. The effect of time and power of sonication on the sufficient dispersing of the solid kaolin sample in distilled water (10 wt. %) is evident from Table 2. The best dispersion and therefore, the smallest particles, was achieved by sonication for 10 minutes and 100 % output power of ultrasonic processor UP400S. These conditions were used for subsequent analysis of kaolin dispersion.

The next research was focused on the determination of the possibility to use dispersing tanning agent to reduce the particle coagulation. These dispersing tanning agents were used: solution of
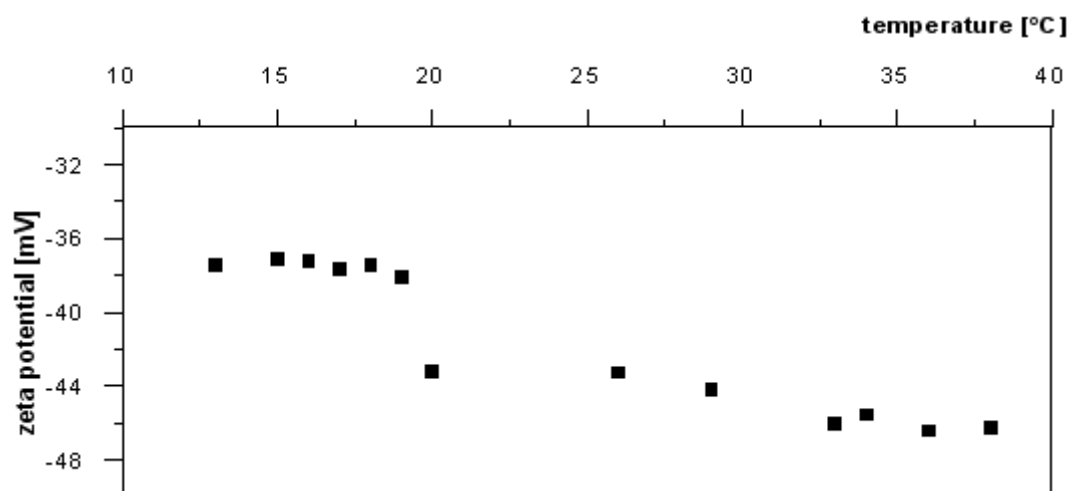

Fig. 8. Effect of temperature on the values of zeta potential (kaolin/0.01M KCl)

Table 2. Effect of sonication on the particle size distribution of kaolin dispersion in H_2O

Output power[%]	Time of sonication [min]	Peak maximum d1		Peak maximum d2	
		Mean [mm]	Std. error [mm]	Mean [mm]	Std. error [mm]
50	2	0.85	0.02	10.61	0.129
	5	0.45	0.077	5.52	0.809
	10	0.34	0.111	5.52	1.003
100	2	0.2	0.028	5.6	0.543
	5	0.25	0.039	6.11	0.641
	10	0.15	0.016	4.41	0.366

Table 3. Effect of dispersing tanning agents on the particle size distribution of kaolin slurry

Dispersing tanning agent	Peak maximum d1		Peak maximum d2	
	Mean [mm]	Std. error [mm]	Mean [mm]	Std. error [mm]
Na_2SiO_3	0.22	0.032	6.35	0.687
$(NaPO_3)_6$	0.32	0.02	8.18	0.445
$Na_4P_2O_7$	0.13	0.005	3.17	0.082
Busperse	0.14	0.025	3.07	0.27

Na_2SiO_3, solution of $(NaPO_3)_6$, solution of $Na_4P_2O_7$ and commercial dispersing product "Busperse". Concentration of all solutions was 1 g.l^{-1}. Results given in Table 3 show that solutions of Na_2SiO_3 and $(NaPO_3)_6$ do not disperse the kaolin slurry more effective, especially; do not reduce the value of mean d2. Better dispersiveness and almost similar results were obtained by measuring of kaolin slurry in solutions of $Na_4P_2O_7$ and Busperse. These dispersing tanning agents are suitable for preparation of representative sample of kaolin slurry.

Monitoring the dispersion stability is expressed by the measuring of particle size distribution of the kaolin slurry in H_2O during 12 days time period. During the first 4 days the slurry was quite stable and the values of means d1 and d2 were almost constant (Fig. 9, 10). The coagulation of particles was found out after the fifth day. The value of mean d1 increased at about 200 % and its trend was cumulative until the end of the analysis. The value of mean d2 also rapidly increased starting with the fifth day of testing, for the next 10 days was constant.
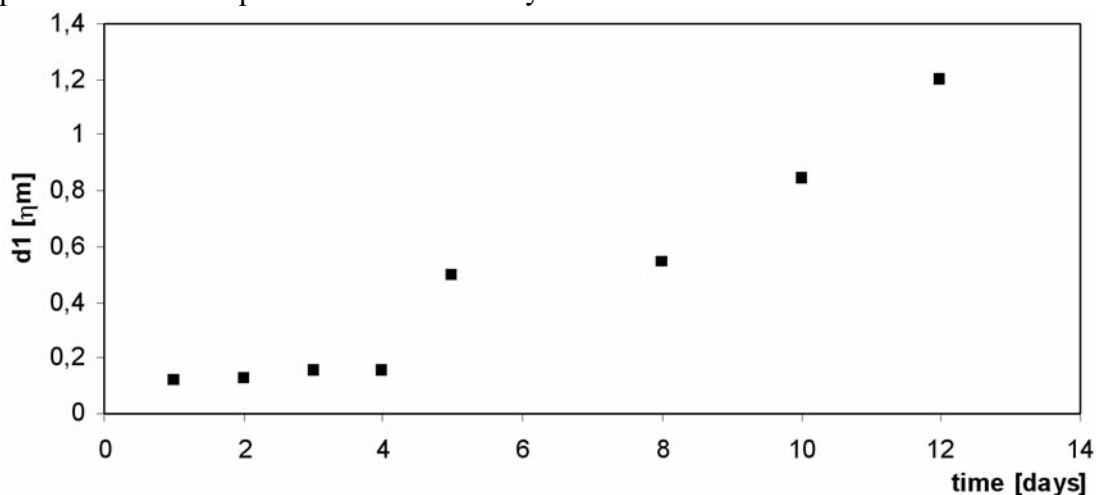

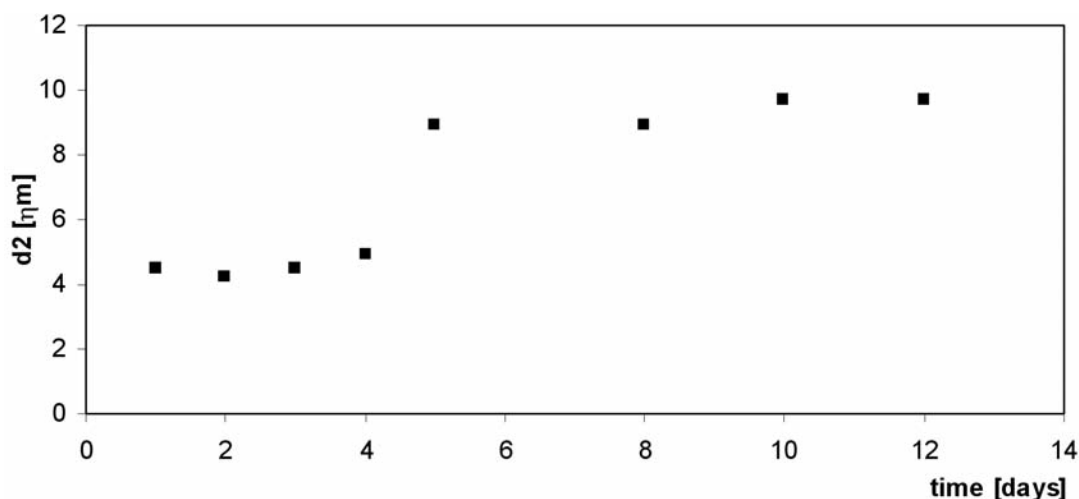*Fig. 9. Change the mean particle size d1 of kaolin during the time period*

Fig. 10. Change the mean particle size d2 of kaolin during the time period

4. Conclusion

The behaviour of the aqueous slurries is the actual problem in modern experimental research of the ceramic industry. The coagulation of particles can be followed up and described by measuring of electrokinetic properties such as the zeta potential. The present work was focused on preparation of stable concentrated kaolin aqueous slurry and its analysis. Results show that the appropriate concentration of solid particles of kaolin in liquid medium for analysis by ultrasonic spectrometer DT-1200 is minimally 7.5 wt. %. The isoelectric point of 10 wt. % kaolin slurry is about pH_{IEP} = 3.5-4.5, depending on electrolyte solution. The values of pH_{IEP} of the kaolin suspensions increase in the order of solutions H_2O (3.60) – KCl (3.75) – $CaCl_2$ (3.98) and $MgCl_2$ (4.50). The system kaolin/H_2O shows higher stability in temperature interval from 20 to 38 °C.

The particle size distribution of the tested kaolin powder is polydisperse and contains two size maximum peaks. The best dispersing was achieved by sonication for 10 minutes and 100 % output power of ultrasonic processor UP400S. These conditions brought values of mean d1=0.15 µm and d2=4.4 µm stable for 4 days. Better momentary dispersion brought the commercial dispersing tanning agent "Busperse" and solution of $Na_4P_2O_7$ (1 g.l^{-1}).

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