Investigation of Removal Possibilities of Colloidal Alumina from Aqueous Solution by the Use of Anionic Polyacrylamide

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ABSTRACT: Purification of drinking and industrial water required usage of high molecular weight polymer to cause flocculation process of dispersed suspension of contaminants. Polyelectrolytes, including ionic polyacrylamide are especially appropriate for these purposes, because in this case the suspension stability can be controlled by both steric and electrostatic forces. Thus the influence of solution pH and hydrolysis degree (carboxyl groups content) of anionic polyacrylamide (PAM) on the alumina (Al_2O_3) suspension stability were studied. The turbidimetry was applied for determination of the examined systems stability. The mechanism of suspension stabilization or destabilization in the polymer presence was proposed on the basis of determined parameters: adsorbed amount of PAM, its adsorption layer thickness, linear dimensions of macromolecules in the solution and zeta potential of alumina particles covered with the polyacrylamide layer. The greatest decrease of the alumina suspension stability in the polymer presence in comparison to that without the polymer was obtained at pH 6 after the addition of PAMs with higher molecular weight (i.e. 14 000 0000) and hydrolysis degrees 20 and 30% (efficient neutralization of solid surface charge). In turn, the most unstable alumina system proved to be that prepared at pH 9 containing PAM with the highest molecular weight and the greatest hydrolysis degree (causing the most effective bridging flocculation).

Key words: Alumina removal, Anionic polyacrylamide, Carboxyl groups content, Suspension stability, Polymer chains conformation.

INTRODUCTION

Adsorption process of various substances (low- and macromolecular) on the solid surface (Nosal-Wiercińska and Dalmata 2010; Yang and Qiu 2010; Nosal-Wiercińska and Grochowski 2011; Cigdem *et al.* 2012; Nosal Wiercińska 2012; Grządka 2013; Kaźmierczak *et al.* 2013; Nowicki *et al.* 2015) has found a wide usage in many areas of human activity. Water soluble polymers have proven to be very effective agents significantly changing the surface properties of many adsorbents. Depending on the specific needs of practical application, obtaining highly stable systems is required, or on the contrary, the process of effective destabilization of the suspension is necessary. The first case takes place in the production, among others, of: paints, cosmetics and drugs, as well as in food processing (Shahidi *et al.* 1999; Tadros 2008; Gurumoorthy and Kha 2011). In turn, the processes of industrial wastewater and drinking water purification use the effect of considerable reduction in the suspension stability in the presence of a polymer, resulting from the flocculation. This process is of significant importance in ecology, as one of the stages of purification of wastewaters in the form of aqueous colloidal suspensions (Jin *et al.* 2003; Tripathy and De 2006; Sojka *et al.* 2007; Haydar and Aziz 2009).

Two most important types of flocculation are bridging (Yu *et al.* 2006; Kamibayashi *et al.* 2008; Proskurina and Myagchenkov 2009) and depletion ones (Besra *et al.* 2002; Witham *et al.* 2012).

Bridging flocculation occurs when the long polymer chains form bridges between the colloidal particles. Such bridge can create a macromolecule adsorbed on the surface of two or more colloidal particles. The second possible type of bridging flocculation consists in the fact that two macromolecules adsorbed on two different colloidal particles participate in bridge formation. Bridging flocculation occurs usually at low concentrations of polymer in solution, and hence at the partial coverage of the particle surface with the adsorbed

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macromolecular substance. In turn, depletion flocculation is the aggregation of solid particles in the presence of free macromolecules, non-adsorbing on the solid surface which occurs at high concentrations of polymer in the system.

The main aim of this study is to describe the mechanism of stabilization or destabilization of the alumina suspensions in the presence of the anionic polyacrylamide (PAM). Research of such systems very often focused on determining whether a suspension is stable or not, without giving any explanation why this is so. For this reason, our research will deal with determination of firstly metal oxide suspension stability in the presence of polyacrylamide, and secondly, giving the precise characteristics of possible processes occurring at the interface, which are responsible for the specific behaviour of these systems. To accomplish this it is necessary to determine the conformation of polymer chains, which directly influences the structure of the polymer adsorption layer, and thus the stabilization-flocculation properties of such suspension in the presence of the polymer.

Additionally, the goal of this paper is verification of the statement (commonly found in the literature) that destabilization of colloidal suspension is caused by the polymers with high molecular weight (of the order of several million), whereas polymers with low molecular weights (the order of thousands) are stabilizers of such systems. This seems to be significant simplification. Therefore our research is focused on proving the fact that the polymer molecular weight is not the most important factor influencing the stability of colloidal suspension, but this effect is also dependent on other parameters (related to the type of polymer and adsorbent, functional groups content in macromolecules, degree of their dissociation and solution pH).

MATERIALS & METHODS

γ-Al_2O_3 (Merck) was used in the experiments as an adsorbent. The aluminum (III) oxide was washed with doubly distilled water (to achieve the supernatant conductivity less than 2 μS/cm). The BET specific surface area of Al_2O_3 was equal to 155 m^2/g (Micrometritics ASAP 2405 analyzer). The average pore diameter of the alumina was 6.1 nm. The mean grain size of the solid particles was 496 nm (Zetasizer 3000, Malvern Instruments). Additionally, the mean diameter of solid particles was measured using high resolution scanning electron microscope Quanta 3D FEG (FEI firm) (Wiśniewska *et al.* 2014). The mean size of alumina particles was 444 nm (good agreement with electrokinetic data). The pH_{pzc} (pzc-point of zero charge) of Al_2O_3 surface was 7.8 (Chibowski *et al.* 2010).

Anionic polyacrylamide -PAM (Korona) samples with the weight average molecular weights 11 000 000 and 14 000 000 were applied as an adsorbate. Their macromolecules contain two types of functional groups: the amide (-$CONH_2$) and carboxyl (-COOH) ones. These latter groups are formed during the production of this compound by hydrolysis of a number of amide groups. The degrees of PAM samples hydrolysis were specified by the producer and were as follows: for PAM 11 000 000 – 5%, for PAM 14 000 000 – 20 and 30%. In this paper, three used polyacrylamides are marked as: 11 000 000_5%, PAM 14 000 000 – 20% and PAM 14 000 000 – 30%.

Amide groups do not undergo dissociation. The negative charge of PAM macromolecules comes from dissociation of the -COOH groups, which strongly depends on the solution pH. The higher the pH value is, the greater number of negatively charged carboxyl groups appears in PAM chains.

Stability, viscosimetry and electrokinetic measurements were carried out at 25°C at the three different solution pH values: 3, 6 and 9. NaCl ($1 \cdot 10^{-2}$ mole/dm^3) was used as the supporting electrolyte.

The pH was adjusted using pH-meter PHM 240 (Radiometer) with accuracy ±0.1. The HCl and NaOH solutions with concentration $1 \cdot 10^{-1}$ mole/dm^3 were applied for this purpose.

The stability measurements of the alumina-PAM systems were carried out using Turbiscan Lab[Expert] with the cooling module TLAb Cooler. Two synchronized detectors register: the transmission (light passing through the probe at the angle 0° in relation to the incident light direction) and the backscattering (light scattered at the angle 135°). The obtained data are stored and converted by the computer program. The results are presented in the form of intensities of transmission and backscattering (both expressed in %) as a function of time.

The analyzed suspension in a glass phial (7 cm in length) was placed in a thermostated measurement chamber. The suspension with 0.02g of oxide in 20 cm^3 of NaCl solution was sonicated for 1 min (Sonics, LABO PLUS) with frequency 20kHz and 40% of maximal power (equaled 750W). Then the required pH of the solution was adjusted. The suspension was shaken in a water bath (OLS 200, Grant) for 30 min (123-123 pulses/min) and during this time its pH was checked. The changes in the suspension stability were monitored for 15 h (single scans were collected every 15 min). The probes of the alumina suspension containing polyacrylamide were prepared in a similar way. An appropriate volume of the basic PAM solution (with the concentration 1100 ppm), providing its final

concentrations 10, 50 and 100 ppm, was added to the suspension after sonication.

The transmission and backscattering data enable calculation of the following stability parameters: the stability coefficient TSI (Turbiscan Stability Index), the thickness of formed sediment s [mm] and the rate of particles (aggregates, flocks) migration V [µm/min]. These data were calculated using the programs TLab EXPERT 1.13 and Turbiscan Easy Soft.

The sample stability can be estimated using TSI. This parameter takes into account all single measurements during experiments and the TSI value is obtained from their averaging.

All processes taking place in the sample including thickness of sediment and clear layer as well as dynamics of particles settling were summed up. The following formula was used to calculate the stability coefficient:

$$TSI = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{BS})^2}{n-1}} \tag{1}$$

where: x_i – average backscattering for each minute of measurement, x_{BS} – average x_1, n – number of scans (repetitions of single measurement during the total time of the experiment).

The TSI values change in the range from 0 to 100 and the higher its value is the more unstable the suspension is. TSI represents the average stability of the system during the experiment.

The thickness of the polymer adsorption layers (δ) was determined from the viscosity measurements (M'Pandou and Siffert 1987) using a CVO 50 rheometer (Bohlin Instruments). For this purpose the following dependencies were used:

$$\delta = r\left[\left(\frac{\phi_p}{\phi_0}\right)^{1/3} - 1\right] \tag{2}$$

where: r radius of the solid particle, ϕ_0 volume fraction of the solid without polymer, ϕ_p volume fraction of the solid with polymer.

$$\frac{\eta}{\eta_0} = 1 + k\phi_0 \tag{3}$$

where: η viscosity of the suspension, η_0 viscosity of the liquid phase, k Einstein coefficient.

In order to prepare a calibration curve there were prepared a few suspensions differing in volume fractions of aluminium oxide (ϕ_0). The obtained suspensions were shaken for 24 h and then viscosities of suspension (η) and the viscosity of clean mother solution (η_0) were measured. Thus the relation (η/η_0) in the function ϕ_0 was obtained. Measurements of viscosity of the suspension with the adsorbed polymer were performed in an analogous way with the volume fraction of Al_2O_3 $\phi_0 = 0.94\cdot10^{-3}$. Knowing the radius of aluminium oxide particle and the value of solid volume fraction in the presence of polymer (ϕ_p) found on the calibration curve, there was determined adsorption layer thickness from the equation [2].

The ϕ_p values obtained from calibration curve are listened in Table 1. As can be seen, for all examined systems the increase of the solid volume fraction with adsorbed PAM in comparison to that without polymer (ϕ_p/ϕ_0) is observed.

From the viscosity data there were also calculated the root-mean-square chain end-to-end distance ($\overline{r^2}$)$^{1/2}$ and the hydrodynamic radius of a polymer coil in the solution R_h. These parameters were obtained from the expressions:

$$\left(\overline{r^2}\right)^{1/2} = \left(\frac{[\eta]M}{F}\right)^{1/3} \tag{4}$$

where: [η] intrinsic viscosity of the polymer solution at a given temperature, F universal Flory-

Table 1. The alumina volume fractions with adsorbed polyacrylamide (ϕ_p) and the ratios of ϕ_p/ϕ_0 (ϕ_0=0.94·10⁻³).

System	pH	ϕ_p	ϕ_p/ϕ_0
	3	$0.997\cdot10^{-3}$	1.056
Al_2O_3 – PAM 11 000 000_5%	6	$1.050\cdot10^{-3}$	1.111
	9	$1.138\cdot10^{-3}$	1.205
	3	$1.029\cdot10^{-3}$	1.089
Al_2O_3 – PAM 14 000 000_20%	6	$1.090\cdot10^{-3}$	1.154
	9	$1.215\cdot10^{-3}$	1.285
	3	$1.057\cdot10^{-3}$	1.119
Al_2O_3 – PAM 14 000 000_30%	6	$1.115\cdot10^{-3}$	1.180
	9	$1.250\cdot10^{-3}$	1.324
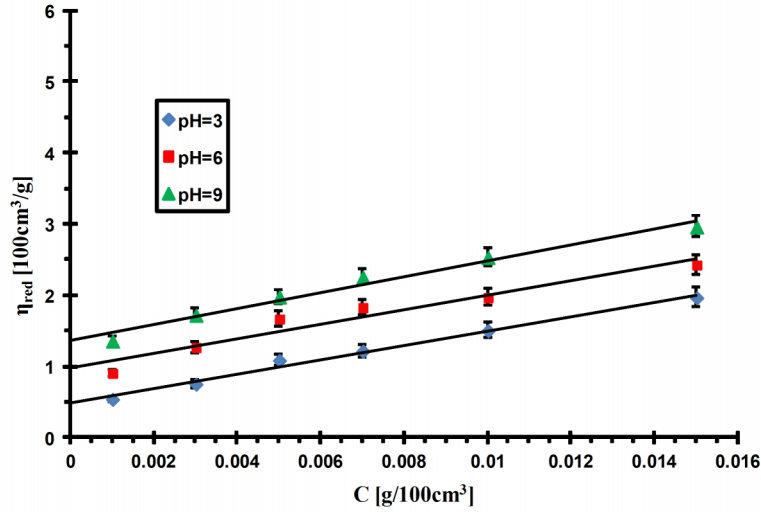
Fig. 1. Reduced viscosity of PAM 11 000 000_5% solution as a function of its concentration.

Fox constant approximately equal to $2.1 \cdot 10^{21}$ (for polymers in good solvents) (Flory 1953; Mohanty *et al*. 1987), M polymer molecular weight.

$$R_h = fR_g = f\frac{\left(\overline{r^2}\right)^{1/2}}{6^{1/2}} \qquad (5)$$

where: f constant value irrespective of the polymer molecular weight (for PAM f=0.66 (Garvey and Tadros 1974), R_g radius of gyration.

The initrinsic viscosity [η] was obtained from the plot $\eta_r = f(c)$ by extrapolating the straight line to the concentration of polymer solution (c) equal to zero:

$$[\eta] = \lim_{c \to 0} \eta_r \qquad (6)$$

where: η_r reduced viscosity:

$$\eta_r = \frac{\eta_s}{c} = \frac{\eta_{rel} - 1}{c} = \frac{\frac{\eta_1}{\eta_0} - 1}{c} \qquad (7)$$

where: η_s specific viscosity, η_{rel} relative viscosity, η_1 polymer solution viscosity, η_0 electrolyte solution viscosity.

The exemplary curves, on the basis of which [η] the values for PAM 11 000 000_5% at different solution pH were determined are given in Fig. 1.

The alumina samples for zeta potential measurements were prepared adding 0.03 g of Al_2O_3 to 500 cm³ of the supporting electrolyte solution (C_{NaCl}=$1 \cdot 10^{-2}$mole/dm³). This suspension was sonicated (ultrasonic processor XL, Misonix) for 5 minutes and

divided into 6 parts. Next, the appropriate pH value (3; 4.5; 5.5; 6.5;8.5 and 10 ±0.1) was adjusted in each sample. The alumina systems in the presence of PAM were prepared in a similar way. For this purpose the appropriate volume of basic polymer was added to the supporting electrolyte solution, which led to its final concentration 1 ppm. The further way of probes preparation was the same as in the case of the solid without the polymer.

The zeta potentials of the alumina particles in the presence and absence of polyacrylamide were measured with the Zetasizer 3000 laser zetameter (Malvern Instruments). To calculation of zeta potential of alumina particles the Smoluchowski equation was used.

The adsorption measurements were made by the static method in the polymer concentration range 5 - 120 ppm at pH values: 3, 6 and 9 (±0,1). 0.1g of Al_2O_3 was added into the Erlenmeyer flask containing 10cm³ of polymer solutions of known concentration and the appropriate pH value was adjusted. Next, it was shaken in a water bath for 3h. Then the solid was centrifuged and 5cm³ of supernatant was taken for analysis. To determine the polymer concentration in the solution, the method proposed by Crummet and Hummel (1963) was applied. 1cm³ of 20% NaOH solution was added to flask containing the PAM solution. Then the sample was heated for 40 min at 90 °C. After this time the solution was cooled to room temperature and its pH was adjusted to the value about 10 (using HCl solutions of the concentrations 1 and $1 \cdot 10^{-1}$ mole/dm³). Next to the PAM solution, prepared in this way, 1 cm³ of 1% solution of hyamine 1622 (benzethonium chloride,

UPAC: N-benzyl-N,N-dimethyl-2-{2-[4-(2,4,4-trimethylpentan-2-yl)ethoxy}ethanaminium chloride) was added and after that the sample was diluted with redistilled water to a volume of 25 cm^3. The solution turbidity (obtained as a result of hyamine addition) was measured after 15 min using the UV-VIS spectrophotometer (Carry 1000;Varian) at 500nm. The amount of the adsorbed polymer was determined from the difference between the PAM concentration in the solution before and after the adsorption process (using the calibration curve prepared earlier).

RESULTS & DISCUSSION

Stability of the alumina suspension in the anionic polyacrylamide presence

Figs. 2 and 3 present the examples of transmission and backscattering curves obtained for the two selected systems, i.e. Al_2O_3-NaCl at pH 3 and Al_2O_3-NaCl-PAM 14 000 000_30% at pH 9 (C_{PAM}=100ppm). Among all investigated suspensions, the first one is characterized by the highest stability and the latter one is the most unstable system.

The level of suspension in the measurement phial is along the x axis and the transmitted and backscattered light intensities [%] are along the y axis. The value of 40 mm on the x-axis in these figures is the mark to which the investigated suspension was poured into the measuring phial. Each stability measurement was 15 hours long and a single scan was collected every 15 min (various colours of the curves correspond to successive scans). The backscattering intensity increases in the direction from top to bottom of the phial and reaches the maximum in the sediment layer. In the case of transmission, the trend is reversed – the transmission level increases from bottom to top of the phial and achieves the maximum in the clear surface layer. The presence of the backscattering peaks is the evidence of the sedimentation process of formed aggregates or flocks (the width of this peak indicates the thickness of sediment layer). On the other hand, the transmission peaks are directly related to the presence of a clear suspension (the width of this peak correlates with the thickness of clear layer on the top of phial.

As can be seen in Fig. 2 the widths of transmission and backscattering peaks are quite small, which reflects the relatively high stability of the Al_2O_3-NaCl system at pH 3. Moreover, the transmission to level of 32 mm does not change in the time of experiment and backscattering curves are close to each. This indicates that the dynamics of processes occurring in this system is rather low - the migration rate of solid aggregates is small.

A completely different situation occurs in the system Al_2O_3-NaCl-PAM 14 000 000_30% at pH 9 (Fig. 3). It is a very unstable suspension, the evidence of which is a very wide backscattering peak – a thick sediment is formed in this system. Additionally, the transmission curves are distinctly separated from each other, their position changes in the time of experiment. This is the evidence of gradual process of suspension clarification and in this case the velocity of flocks migration is rather high.

The good confirmation for these phenomena are the stability parameters: stability coefficient (TSI), sediment layer thickness (s) and migration velocities of aggregate (flicks) migration (V). Their values for all
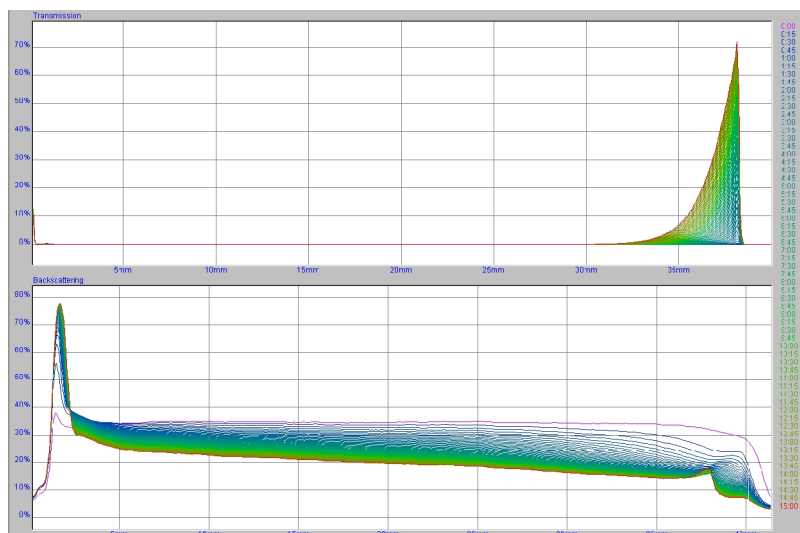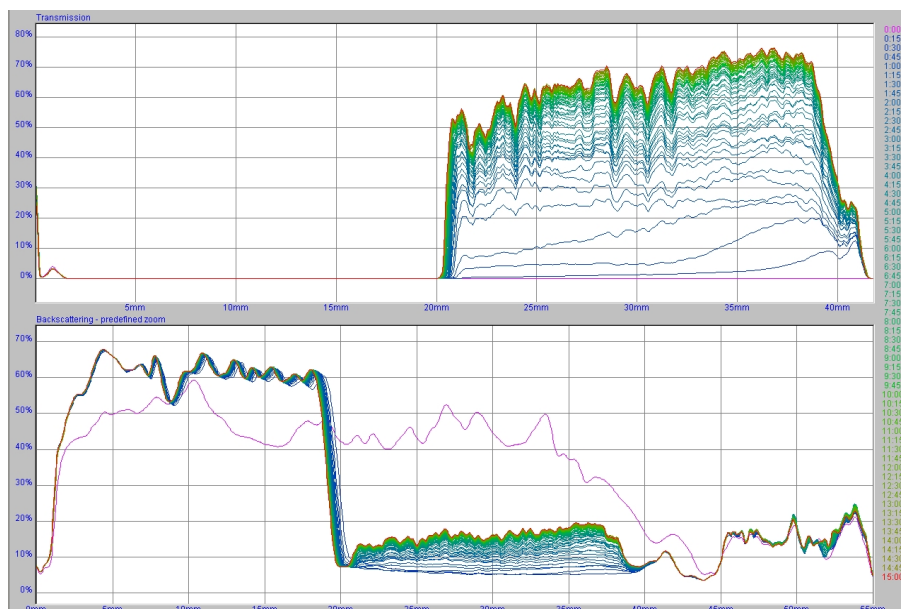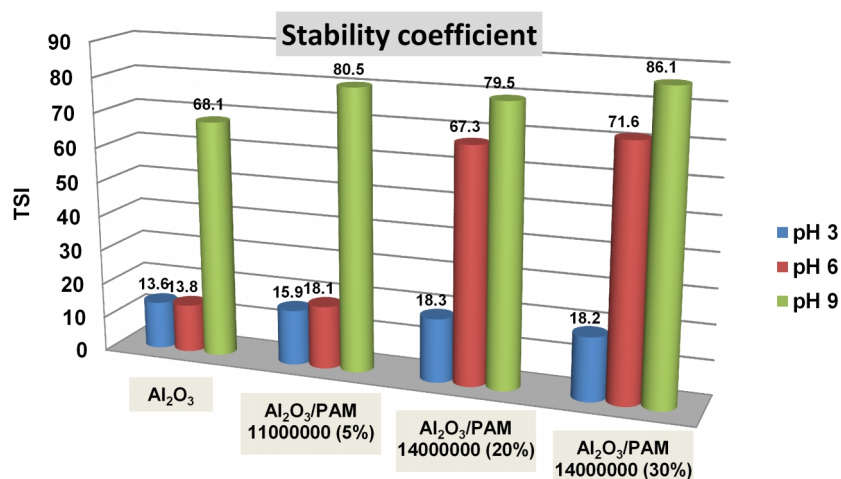

Fig.2. Transsmision and backscattering curves for the alumina suspension without PAM at pH 3, C$_{PAM}$=100ppm.

Fig.3. Transsmision and backscattering curves for the alumina suspension with PAM 14 000 000_30% at pH 9, C_{PAM}=100ppm.

Fig.4. Stability coefficient (TSI) for the alumina suspensions in the absence and presence of PAM at different solution pH values, C_{PAM}=100ppm.

investigated systems are presented in Figs 4-6, respectively. As can be seen in Fig. 4, the alumina suspensions without PAM at pH 3 and 6 are the most stable systems (TSI = 13.64 and 13.77, respectively) of all examined ones. Its stability dramatically decreases at pH 9 (TSI = 68.03). The obtained values of stability coefficients correspond with the sediment thickness (Fig. 5) and aggregate migration velocity (Fig. 6). In the case of Al_2O_3 suspension at pH 3 and 6 thin sediment layers are formed on the phial bottom (less than 1 mm) and also the velocities of particle migration are small (0.3-0.4 μm/min). At pH 9 these parameters noticeably increase to the values 2.49 mm and 0.57 μm/min.

The polyacrylamide addition to the alumina suspension at pH 3 (independently of its molecular weight and hydrolysis degree) causes a minimal decrease of its stability – the system remains still comparatively stable (TSI in the range 16–18). Simultaneously, thickness of the formed sediments (s) and flock migration velocities (V) increase slightly (s in the range 1.18-1.74 nm and V: 0.34-1.68 μm/min). A completely different situation occurs at pH 6, at which after the addition of PAM 14 000 000 (irrespective of its hydrolysis degree), the solid suspension undergoes substantial destabilization (TSI = 67.26 and 71.61 for PAM 14 000 000_20% and PAM 14 000 000_30%,
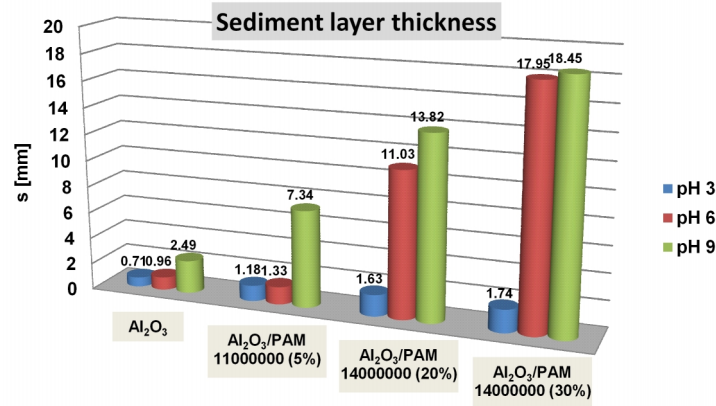
Fig.5. Thickness of sediment layer (s) for the alumina suspensions in the absence and presence of PAM at different solution pH values, C_{PAM}=100ppm.
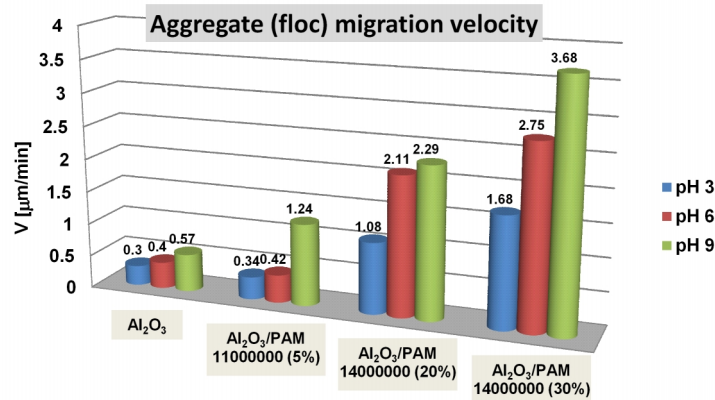

Fig.6. Aggregate (floc) migration velocity (V) for the alumina suspensions in the absence and presence of PAM at different solution pH values, C_p=100ppm.

Table 2. The number of polymer segments adsorbed on 1 nm^2 of the solid surface.

System	pH	N [seg/nm^2]
Al_2O_3 – PAM 11 000 000_5%	3	0.71
	6	0.46
	9	0.14
Al_2O_3 – PAM 14 000 000_20%	3	0.87
	6	0.50
	9	0.17
Al_2O_3 – PAM 14 000 000_30%	3	1.87
	6	0.62
	9	0.24

respectively). The corresponding values of s and V parameters for these two polymers also increase considerably to 11 and 18 mm (thickness of sediments) and 2.11 and 2.75 μm/min (flock migration velocities). Only polyacrylamide with a lower molecular weight, i.e. PAM 11 000 000_5% changes minimally the stability of the alumina suspension towards its slight decrease (TSI=18.09; s=1.33 mm; V=0.42 m/min). The polymer presence in the aluminum (III) oxide system at pH 9

contributes to further destabilization of the suspension, which was already unstable before the polymer addition (TSI increases in the range 80-86). The higher is the polymer molecular weight (and its hydrolysis degree), the larger suspension destabilization takes place. At pH 9 the thickest sediment layers in the polymer presence are formed (7-18 mm) and the velocity of flock migration reaches the value 3.68 μm/min for the alumina suspension containing PAM 14 000 000_30%.
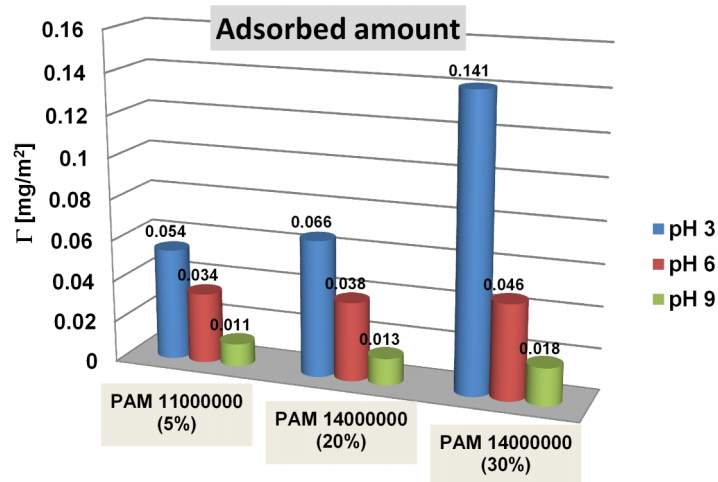
Fig.7. Adsorbed amount (Γ) of PAM on the alumina surface at different solution pH values, C_{PAM}=100ppm.

Table 3. Characteristic of linear dimensions of PAM macromolecules in the solutions of different pH.

Polymer	pH	$[\eta]$ [100cm^3/g]	$\overline{(r^2)}^{1/2}$ [nm]	R_h [nm]
	3	0.6	65.8	17.7
PAM 11 000 000_5%	6	0.99	77.8	20.9
	9	1.35	86.3	23.2
	3	0.8	72.5	19.5
PAM 14 000 000_20%	6	1.2	82.9	22.3
	9	1.7	93.2	25.1
	3	0.9	75.4	20.3
PAM 14 000 000_30%	6	1.35	86.3	23.2
	9	1.82	95.8	25.8

Structure of polyacrylamide adsorption layer on the Al$_2$O$_3$ surface

In order to explain the observed changes in the stability of the alumina suspensions without and with polyacrylamide very helpful is knowledge about the adsorption behaviour of the polymer at the solid – liquid interface, and the conformation of its macromolecules in the bulk solution and on the surface. The detailed characteristics of the PAM adsorption mechanism on the Al$_2$O$_3$ surface (adsorption isotherms) as a function of solution pH was given in our separate paper (Wiśniewska *et al.* 2015). In the present manuscript we limit ourselves to show the adsorbed amounts of PAM (at its initial concentration before adsorption 100 ppm) at different solution pH values. These data are presented in Fig. 7 and they are necessary to explain the obtained stability dependencies. Moreover, the numbers of polymer segments adsorbed on 1 nm^2 of the solid surface were calculated and placed in Table 2.

Additionally, Fig. 8 illustrates the thickness of polymer adsorption layers and Table 3 presents the parameters characterizing linear dimensions of polymer chains in the solution.

Their analysis indicates that the increasing solution pH causes decrease of polyacrylamide adsorption (smaller number of polymeric segments are adsorbed on the 1 nm^2 of surface area) and formation of thicker adsorption layer of the polymer. It results from the changes in both dissociation of carboxyl groups in the polymer chains and charge of the solid surface with the pH rise. Due to the fact that pH$_{pzc}$ of Al$_2$O$_3$ is 7.8 (Wiśniewska *et al.* 2014), at pH 3 its surface is charged positively, at pH 6 - also positively (but the surface charge density is smaller than that at pH 3) and at pH 9 the alumina surface is negatively charged. On the other hand, the rise of the pH value causes the increase of the number of negatively charged carboxyl groups located along the PAM chains. It leads to the increase of electrostatic repulsion between –COO$^-$ groups within the same and neighbouring macromolecules resulting in development of polyacrylamide chains. The evidence of this are the increasing values of
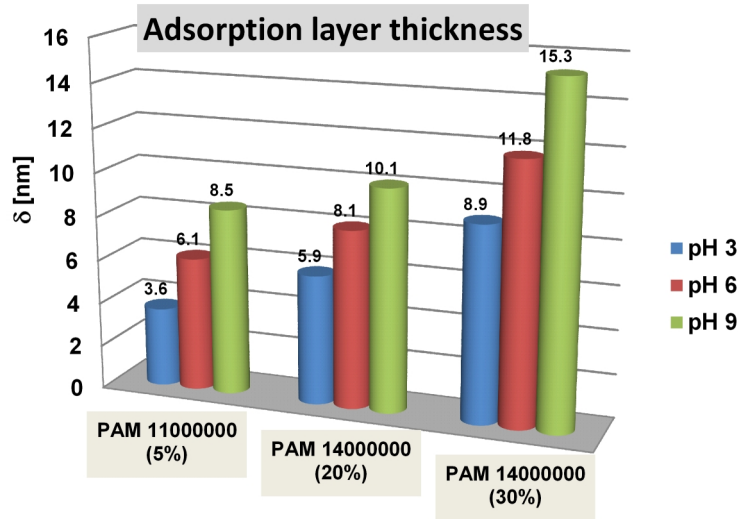
Fig.8. Adsorption layer thickness (δ) of PAM on the alumina surface at different solution pH values, C_{PAM}=100ppm.
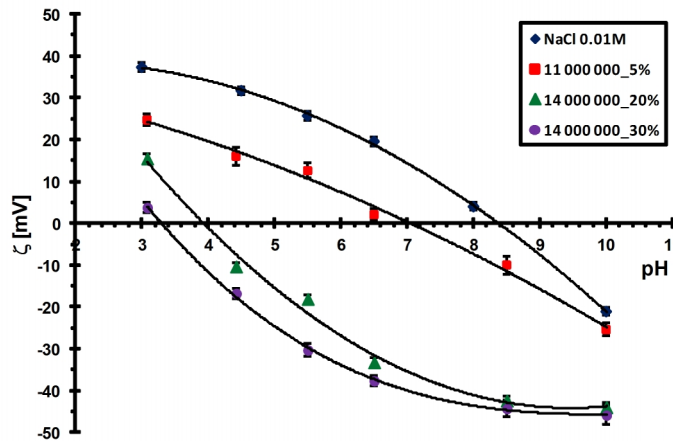

Fig.9. Zeta potential (ζ) of the alumina particles in the absence and presence of PAM at different solution pH values.

parameters ($(\overline{r^2})^{1/2}$ and R_h) describing linear dimensions of polymer macromolecules in the solution with the pH rise (Table 2). Such tendency was obtained for all examined polyacrylamides. The higher molecular weight of PAM is (or the higher degree of its hydrolysis for the same molecular weight is), the larger development of polymer chains in the bulk solution is obtained. The similar conformational changes of PAM macromolecules with the pH rise occur in the adsorption layer. Nevertheless, in such a case the alumina surface charge has the additional effect on the polymer chain conformation. As a result of polymer segments binding to the alumina surface, the conformation of the adsorbed macromolecules is flatter than that in the bulk solution. The evidence of this is

comparative analysis of the thickness of PAM adsorption layer (δ) formed on the solid surface and the corresponding hydrodynamic radius of macromolecule (R_h) in the solution. In the case of all examined polymers, R_h assumes greater values than δ.

Taking the above into consideration, one should note that the adsorbing PAM chains at pH 3 have a more coiled structure (small dissociation of its carboxyl groups). The electrostatic attraction between the polymer macromolecules (slightly negatively charged) and the positively charged solid surface leads to the formation of densely packed adsorption layer composed of polymeric coils. As a result, the highest adsorption of PAM and the thickest adsorption layer of the polymer at pH 3 were obtained.

Table 4. TSI indexes for alumina suspensions in the presence of PAM with different concentrations.

System	C_{PAM} [ppm]	TSI	
		pH=3	pH=9
Al$_2$O$_3$ – PAM 11 000 000_5%	10	25.9	65.4
	50	20.7	72.7
	100	15.9	80.5
Al$_2$O$_3$ – PAM 14 000 000_20%	10	22.9	40.5
	50	18.7	61.8
	100	18.3	79.5
Al$_2$O$_3$ – PAM 14 000 000_30%	10	23.2	57.2
	50	22.6	85.0
	100	18.2	86.1

At pH 6 the conformation of adsorbed chains is more developed (significant dissociation of carboxyl groups), which leads to binding a smaller number of PAM macromolecules with the still positively charged alumina surface compared to that at pH 3. This leads to polyacrylamide adsorption lowering and formation of thicker adsorption layer at pH 6.

In turn, at pH 9 there occurs the electrostatic repulsion between the totally dissociated PAM chains and the negatively charged solid surface. Such unfavourable interactions result in the smallest polymer adsorption and the thickest adsorption layer formation (considerable development of adsorbed chains in the perpendicular direction to the solid surface due to the adsorbent-adsorbate repulsion). The adsorption of PAM on the Al$_2$O$_3$ surface at pH 9 proceeds through the hydrogen bridges (Kasprzyk-Hordern 2004).

Taking into account the adsorption behaviour of PAM on the alumina surface and the stability data, the most probable mechanism of polymeric stabilization or destabilization of colloidal suspension can be proposed. The high stability of the alumina suspension in the absence of the polymer at pH 3 and 6 results from sufficiently high absolute values of zeta potential of solid particles. As can be seen in Fig. 9. the zeta potential values are 37 and 25 mV, respectively. In these cases the electrostatic stabilization of the examined systems takes place. In turn, at pH 9 the zeta potential reaches the absolute value of about 10 mV, which is insufficient to ensure effective repulsion between the solid particles. In this situation, coagulation of the alumina suspension occurs.

Due to PAM adsorption a considerable decrease of zeta potential of the alumina system is observed (the zeta potential reduction is the highest for PAM 14 000 000_30%). Two main reasons are responsible for the solid zeta potential changes in the polymer presence: shift of slipping plane away from the solid surface due to polymer adsorption and occurrence of negatively charged polymer carboxyl groups in the diffusion part of the electrical double layer around the alumina particles.

The polacrylamide addition at pH 3 causes minimal stability reduction of the alumina suspension, which still remains relatively stable. For all examined PAMs at pH 3, their maximal adsorption is observed. It follows from the more coiled structure of adsorbed chains, whose carboxyl groups are dissociated to a negligible degree (hence the thinnest PAM adsorption layer is formed). The densely packed adsorption layers of polyacrylamide cover the solid particles and guarantee steric stabilization of the system.

At pH 6 the presence of PAM 11 000 000 slightly deteriorates relatively high stability of the Al$_2$O$_3$ suspension. The considerable dissociation of carboxyl groups in the polymer macromolecules, in the case of their small number (5%) does not give the sufficient neutralization of solid positive charge. The suspension remains stable and its stability results from steric reasons. For PAMs with the molecular weight 14 000 000 (degree of hydrolysis 20 and 30%), the number of –COO$^-$ groups is sufficient to provide the effective neutralization of solid particle positive charge, which is reflected in rapid destabilization of the suspension.

The smallest PAM adsorption and the largest thickness of its adsorption layer at pH 9 causes further destabilization of solid suspension, which was unstable before the polymer addition. The most probable mechanism of this destabilization is bridging flocculation. The process of polymer bridges formation between the alumina particles favours the small surface coverage with the polymer (the smallest PAM adsorption) and large development of the adsorbed PAM chains towards the liquid phase (the thickest polymer adsorption layer). In such a case polymer chains already connected with the surface of other particle can adsorb on the bare parts of solid particle surface (polymeric bridges creation leading to flocks production). It is clear that the higher the degree of

polacrylamide hydrolysis is, the significantly thicker the sediment layer is obtained.

The stability of alumina suspensions containing PAMs with different concentrations is characterized by TSI values, which are placed in Table 4.

Their analysis leads to the conclusion that polymer dosage has some impact on flocculation properties of polyacrylamide (especially at pH 9). At pH 3 stability of suspension containing PAM varies slightly with the increase of polymer concentration. For all PAM samples the tendency of stability conditions improvement with the increase of polymer dosage is observed. The opposite situation takes place at pH 9, at which the destabilization effect rise considerably with the increase of PAM dosage. It was found that the most effective flocculent of the alumina water suspension is anionic PAM characterized by: molecular weight 14 000 000, carboxyl groups content 30%, concentration 100 ppm, and at pH 9. In this case the highest TSI value is obtained, which corresponds with the thickest sediment layer and the fastest migration of formed .

CONCLUSIONS

The solution pH and polyacrylamide hydrolysis degree (carboxyl groups content) influence the alumina suspension stability. Basing on the analysis of all experimental data the most probable mechanism of alumina suspension stability under different conditions was proposed.

The adsorption of polyacrylamide at pH 3 is the highest and the ionization of carboxylic groups in its macromolecules is minimal. The adsorption layer, composed of densely packed polymer coils, is the thinnest, which ensures the steric stabilization of alumina suspension (for all applied PAMs).

At pH 6, the PAM chains adsorbed on the solid surface are negatively charged (substantial dissociation of carboxylic groups). Their content in PAM 11 000 000 macromolecules of 5% is insufficient for neutralization to the solid surface charge and the Al_2O_3 system remains stable (steric mechanism). For PAMs with the molecular weight 14 000 000 (degree of hydrolysis 20 and 30%) the number of $-COO^-$ groups is sufficient to provide the effective neutralization of solid particle positive charge leading to suspension destabilization.

The smallest adsorption of PAM at pH 9 as well as the strong electrostatic repulsion between the negatively charged alumina surface and the totally dissociated polymer chains lead to deterioration of stability conditions in the examined system. In this case there takes place the polymer bridging resulting in suspension flocculation. Polymer bridges formation favours the small surface coverage with the polymer and large development of the adsorbed PAM chains towards the liquid phase (the thickest polymer adsorption layer). The higher hydrolysis degree of PAM is, the greater reduction of suspension stability is observed.

The polyacrylamide 14 000 000_30% with concentration 100 ppm at pH 9 was selected as the most effective flocculent of water alumina suspension. It can be used to remove undesirable colloidal components from industrial and municipal waste.

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