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Effect of polyacrylic acid (PAA) adsorption on stability of mixed alumina-silica oxide suspension

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ABSTRACT

The influence of solution pH and polymer molecular weight on the stability of mixed alumina-silica oxide suspension in the absence and presence of polyacrylic acid (PAA) was studied. The composition of the adsorbent was: Al_2O_3 (96%) and SiO_2 (3%). To obtain changes in the stability of the investigated systems as a function of time the turbidimetry method was applied. It was shown that the suspension without the polymer was characterized by the smallest stability at pH 9, whereas at pH 3 and 6 the systems are successively stable. PAA with the molecular weighs 2000 at pH 3 (large deterioration of system stability conditions) and PAA (all molecular weights) at pH 9 (considerable improvement of suspension stability) have a great effect on the alumina-silica stability. The specific conformation of PAA chains on the solid surface which depends on solution pH and polymer molecular weight is responsible for the stabilization–flocculation properties of polyacrylic acid in the colloidal suspension.

1. Introduction

The state of colloidal dispersion is essential for many technological applications. However, the colloidal particles tend to aggregate due to van der Waals attractions. The polymer addition is a very good way to obtain the improvement of stability conditions of such systems. If polymer chains undergo adsorption on the solid particles the steric repulsion appears leading to steric stabilization [1]. In the case of ionic polymers (polyelectrolytes), besides steric repulsion the electric one occurs. This electric repulsion comes from the charges possessed by the ionized functional groups of macromolecules. Thus the stabilization mechanism is combined, that is electrosteric [2]. On the other hand, ncreasing concentration of unadsorbed macromolecules can also affect the suspension stability causing so called depletion stabilization [3].

The stabilization properties of polymers are widely used in production of paint (i.e. stabilization of titania particles [4,5]), cosmetics [6,7], washing agents (detergents) [8,9], paper [10,11], pharmaceutics (controlled drug delivery) [12,13] and food processing (improvement of taste, smell and consistence) [14,15].

The polymer presence in the colloidal suspension can also cause its destabilization [16,17] manifested in bridging flocculation (adsorbed polymer), particle charge neutralization (adsorbed ionic polymer) or depletion flocculation (unadsorbed polymer). Two mechanisms of bridging flocculation can be distinguished: (1) bridging of particles by one polymer chain attached to both particles, (2) bridging by the interaction of polymer chains attached to different particles.

The most important application of destabilization process in the presence of polymer is industrial and drinking water purification [18,19]. One stage of this operation is to remove suspended solids which cause water turbidity. A properly chosen polymer allows complete separation of suspended solids and the liquid phase is subjected to further stages of purification. For wastewaters containing inorganic compounds anionic flocculants are more effective, whereas for organic substances the cationic ones are preferable.

The polymeric flocculants are also used in petroleum refining [20], mineral processing [21] and textile industry [22].

Such huge demand for efficient stabilizers and flocculants of colloidal suspensions in industry, water treatment and agriculture makes that basic studies of the stability mechanism of solid suspension in the presence of macromolecular compound relevant and necessary.

Thus, the main aim of this work is to determine the changes in stability of mixed alumina-silica oxide suspension in the presence of anionic polyacrylic acid (PAA). Due to the fact that conformation of PAA macromolecule depends on solution pH and polymer molecular weight, their influence was investigated.

2. Experimental

The samples of mixed alumina-silica oxide of the chemical composition: Al_2O_3 (96%) SiO_2 (3%) were used in the study (pilot plant in the Chuiko Institute of Surface Chemistry, Kalush, Ukraine). The alumina-silica suspension will be abbreviated to SA 96. The adsorbent

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was characterized by the BET surface area of 75 m^2/g and the mean pore diameter of 7.4 nm. Both parameters were determined by the low-temperature nitrogen adsorption–desorption isotherm method (Micrometritics ASAP 2405 analyzer). The point of zero charge (pH_{pzc}) of SA 96 was 7.6 (obtained from the potentiometric titration) and its isoelectric point (pH_{iep}) was 8.9 (zeta potential measurements – Zetasizer 3000, Malvern Instruments).

Polyacrylic acid (PAA, Fluka) with the weight average molecular weights 2000, 100 000 and 240 000 were used in the experiments.

All measurements were carried out in the presence of NaCl solution (1×10^{-2}mol dm^3) which was used as the supporting electrolyte. Moreover, the stability experiments were performed at the solution pH 3, 6 and 9 at 25 °C. The polymer concentration was approximately equal to 500 ppm, which provided the surface coverage $\theta=1$. The solid content in the suspensions under investigation was 0.1%.

The stability measurements of silica-alumina suspensions without and with PAA were carried out using Turbiscan Lab^{Expert} with the cooling module TLAb Cooler. This apparatus possesses the electroluminescence diode which emits collimated light beam ($\lambda=880$ nm) passing through the investigated suspension. The apparatus has two synchronized detectors. The transmission detector recorded light passing through the probe at the angle 0° in relation to the incident light direction. The other one is the backscattering detector registering the 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 curves, which show the intensities of transmission and backscattering as a function of time.

The analyzed suspension in a glass phial (7 cm in length) was placed in a thermostated measurement chamber (Fig. 1). The suspension with 0.02 g of oxide in 20 cm^3 of NaCl solution was sonicated for 1 min. Then the required pH of the solution was adjusted. The suspension was shaken in a water bath for 30 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 silica suspension with polyacrylic acid were prepared in a similar way. An appropriate volume of the PAA solution, the desired surface coverage $\theta=1$ ($C_{PAA}\approx500$ ppm), was added to the suspension after sonication.

Based on the transmission and backscattering data the stability parameters were calculated. The stability parameters are: the rate of particles (aggregates, flocs) migration [μm/min], the particle (aggregate, floc) diameters [μm], thickness of formed sediment [mm] and the turbiscan stability index (TSI). These data were calculated using the programs TLab EXPERT 1.13 and Turbiscan Easy Soft. The calculation of migration rate used multiple light scattering theory and the particles diameter calculation was based on general law of sedimentation, that is Stokes' law extended to the concentrated dispersions [23]:

$$V(\varphi,d)=\frac{\left|\rho_p-\rho_c\right|\cdot g\cdot d^2}{18\cdot\nu\cdot\rho_c}\cdot\frac{[1-\varphi]}{\left[1+\frac{4.6\varphi}{(1-\varphi)^3}\right]} \quad (1)$$

where: V — particles migration velocity (μm/min), ρ_c — continuous phase density (kg/m^3), ρ_p — particle density (kg/m^3), d — particle mean diameter (μm), ν — continuous phase dynamic viscosity (cP), φ — volume of dispersed solid fraction (%).

The sample stability can be estimated and compared using turbiscan stability index (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 particles settling were summed up. This coefficient was calculated with the special computer program Turbiscan Easy Soft from the following formula:

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

where: x_i — average backscattering for each minute of measurement, x_{BS} — average x_1, n — number of scans.

The TSI values changes in the range from 0 to 100. The higher the TSI is the more unstable the system is.

The schematic picture of the measuring phial with the suspension and backscattering changes on its different heights are presented in Fig. 1. The backscattering intensity increases in the direction from top to bottom of the phial and reaches the maximum in the sediment layer.

3. Results

Figs. 2–4 present the transmission and backscattering curves of the alumina-silica suspension at different pH in the absence and presence of polyacrylic acid. The level of suspension in the measurement

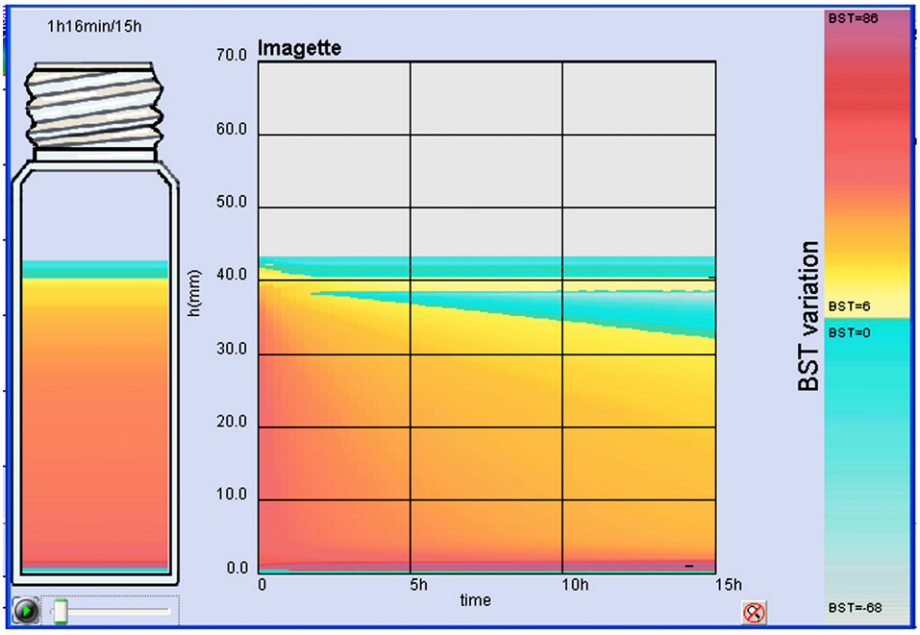

Fig. 1. Schematic picture of measuring phial containing suspension with marked backscattering levels.