Clayed wastewater treatment

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CLAYED WASTEWATER TREATMENT

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Abstract: *Anionic (A120), nonionic (N100), cationic (C460; C581) flocculants and $Al_2(SO_4)_3$ coagulant, were used in purifying clayed wastewater. The pH dispersion was 7.8, with 25.93 kg/m^3 of solids (clays and quartz). 54% of solid particles have less than 10 μm in diameter. The settling rate without any flocculant was 0.4 m/hr. Effectiveness of the used flocculants was: A120>>N100>>C460. In the presence of A120 (100 g/t) the settling rate was about 25 m/hr, the colorless supernatant with the transparency of 98%. The best flocculation result can be explained by the adsorption of A120 on $\equiv AlOH_2^+$ or $\equiv SiOH_2^+$ surface ($\equiv surface$) sites and by the electrostatic interaction on $\equiv Al–O^{\partial-}–H^{\partial+}$ or $\equiv Si–O^{\partial-}–H^{\partial+}$ centres, bridging two or more dispergated particles. A combination of C581 (40g/t) and A120 (100g/t) gave a similar settling rate, but shorter time of sedimentation (3minutes). C581 cations are adsorbed on negative particle surface sites ($\equiv Al–O^-$ or $\equiv Si–O^-$), giving more positive surface centres for adsorption of A120.*

Keywords: *Wastewater, clays, flocculation, zeta potential*

1. INTRODUCTION

It is well known that colloid dispersions are very stable and that solids usually can not be naturally deposited. Adsorbed inorganic electrolytes on dispersed particles affect coagulation by neutralizing the excessive particle surface charges and reducing the repulsive potential of the electrical double layer [1]. Synthetic polymers, mainly polyacrylamides, in aggregation of colloidal particles and suspensions, have been increasingly used in mineral processing and wastewater treatment plants. The adsorbed macromolecules of polymers bridge dispersed particles [2], provoking a special type of coagulation termed „flocculation".

The goal of this paper was to investigate the applicability some flocculants: anionic A 120, nonionic N 100, cationic C 460, (polyacrylamides), and cationic C 581 (polyamine), and coagulant $Al_2(SO_4)_3$ in settling, i.e. in purification of clayed wastewater (the effluent obtained by the washing of clayed quartz sand).

2. EXPERIMENTAL

The clayed wastewater used for investigation was obtained after washing clayed quartz sand of deposit D, Kolubara, Lazarevac. The solid phase (from 2 dm^3 of clayed suspension representative sample) was sieved for a grain size analysis, and the finest size class of -63+0 μm was analysed by beaker decantation method. The density of solid was determined by Beckmann picnometer. The chemical analysis data for the solid phase are given in Table 1.

The flocculation of clayed suspension was carried out using the standard cylinder test to determine the settling rates [3] at natural pH of suspension. Determined volume of standard flocculant solution (0.1%) was added in the cylinder with the representative composite sample (1 dm^3 of suspension). The cylinder was sealed and inverted end-over-end 20 times to ensure complete mixing. The used synthetic flocculants were: anionic A120, nonionic N100, cationic C460 and cationic C581, produced in Cytec Industries Inc., and coagulant $Al_2(SO_4)_3$. The standard solutions of polymers were used within 24 hr of preparation.

Table 1. Chemical analysis of the solid phase

Component	M (%)
SiO_2	59.68
CaO	1.09
MgO	1.31
TiO_2	trace
Fe_2O_3	0.86
Al_2O_3	25.05
LoI	9.32
Σ	97.31

The transparency of supernatant over the precipitate was determined 3 minutes after the subsidence. Three cm^3 of the supernatant was pipette from the depth of 100 cm below the suspension surface, and the transparency was measured on VIS SPECOL spectrophotometer at $\lambda=550$ nm.

A Riddick zeta-meter was used in the microelectrophoretic technique to determine zeta potential. The clayed suspension was stirred for a three minutes after each addition of flocculants and subsidence, and the sample of supernatant colloid was introduced into the electrophoretic cell. The used flocculant concentrations were ten times less than the concentrations used in the sedimentation tests.

3. RESULTS AND DISCUSSION

Clayed waste water (from washing of clayed quartz sand) had pH 7.8. Density of the solid phase and its content in suspension were 2.53×10^3 kg/m^3 and about 25.93 kg/m^3, respectively.

According to the chemical results (Table 1), i.e. to the high Al_2O_3 and SiO_2 contents, the main dispersed components in wastewater seem to be quartz (SiO_2) and clays, i.e. aluminosilicates. Figure 1 shows the grain size composition of the solid phase. Average size of particles in the suspension was about 9 μm. The content of size class -10+0 μm was about 54%.

Colloids (particle diameter 1 nm - 1 μm) are known to naturally settle very slowly, which was proved by the experiment of clayed wastewater sedimentation in the absence of any flocculant. Even after 60 minutes of sedimentation the boundary between the precipitate and the zone above was not clearly notable (after 24 hours this zone was turbid, pale yellow in colour). The settling rate determined from the sedimentation curve approximated 0.4 m/hr (Fig.2, or fig.3, curve 1). The effect of flocculant type and concentration on flocculation efficiency is next studied. Sedimentation curves were used to determine the settling rate for the tested wastewater [3]. Figure 2 shows the relationship between settling rate and flocculant concentration for the flocculants: A 120, N 100 and C 460. The least efficient proved cationic flocculant C 460. Added in concentrations from 40 to 160 g/t this flocculant gave extremely low settling rates (0.75-2.5 m/hr; Fig.2, curve 1). The flocs were very small. Supernatant was turbid 5 minutes after precipitation so that transparency was not determined.

In the presence of nonionic flocculant N100 the results were somewhat better than with C460. With N100 concentration increasing from 50 to 75 g/t the settling rate increased from 2.2 to 8.3 m/hr (Fig.2, curve 2). The settling of medium-sized flocs was faster in the first ten minutes and ceased after thirty minutes. The supernatant had the transparency of about 52%. Concentrations of 100 to 150 g/t N100 had almost no effect on the settling rate, which was about 11 m/hr; only flocs were larger and sedimentation was faster in the first two minutes but ceased twenty minutes after the beginning. The supernatant was colourless, slightly turbid, with transparency of 70%.
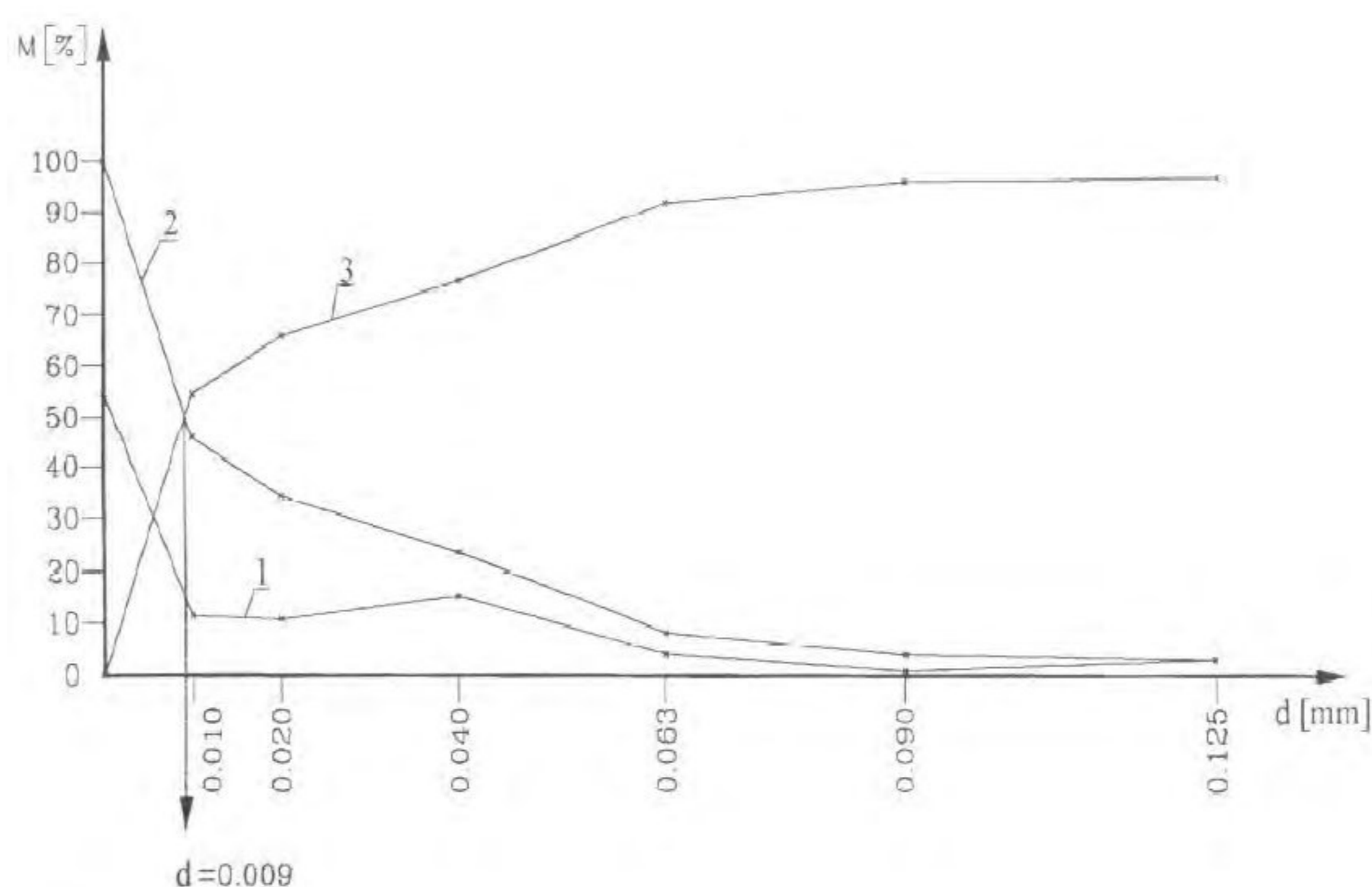
Figure 1. Screen analysis of solid phase: 1) frequency curve; 2) cumulative % oversize; 3) cumulative % undersize.
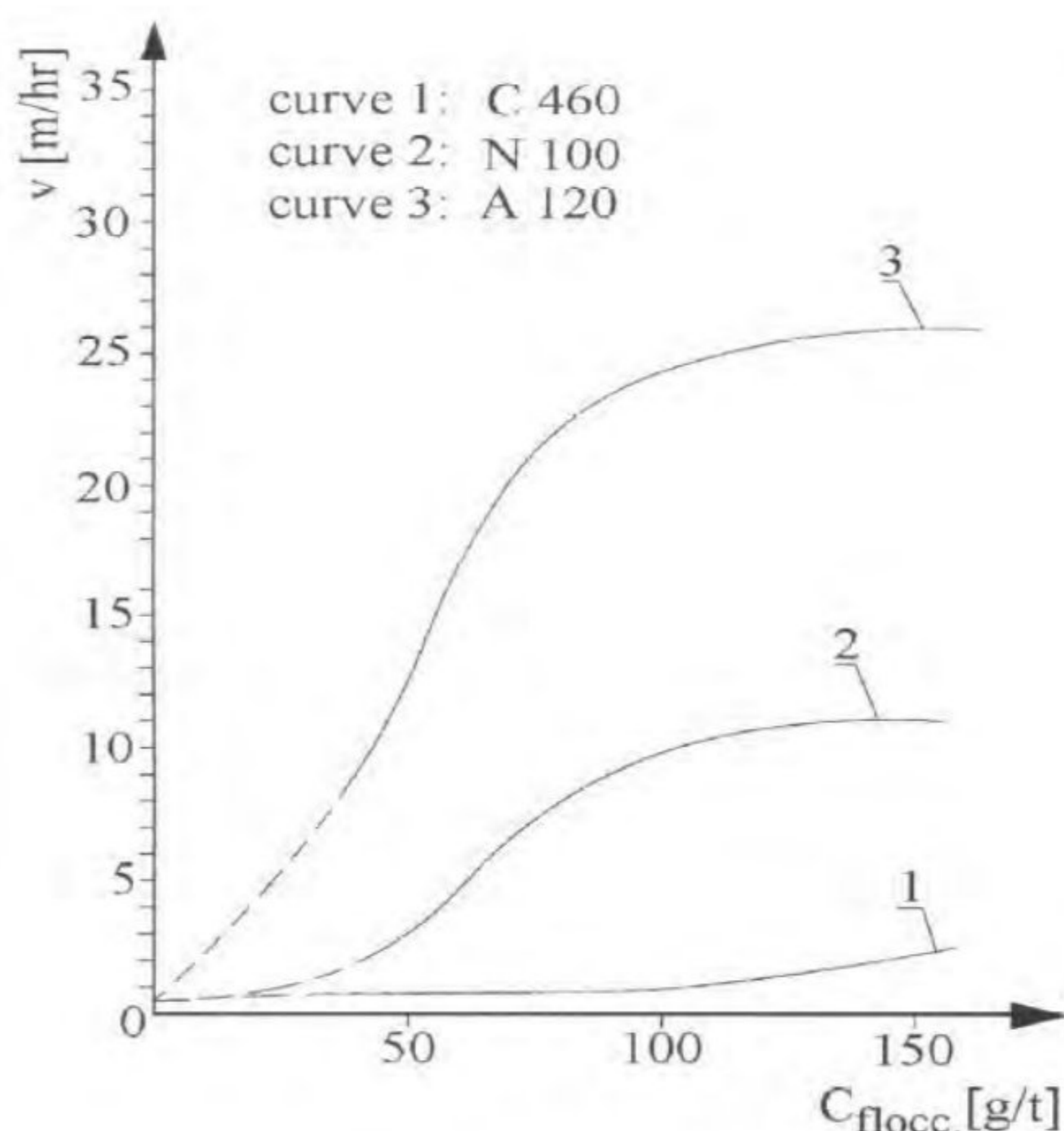

Figure 2. Settling rate of clayed wastewater as a function of flocculant concentration:
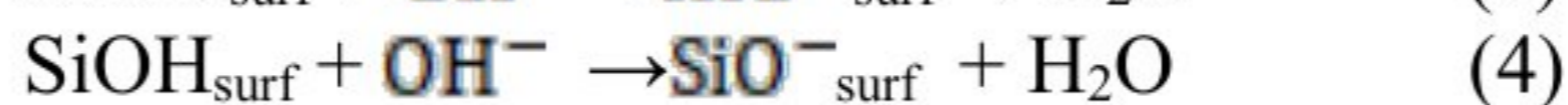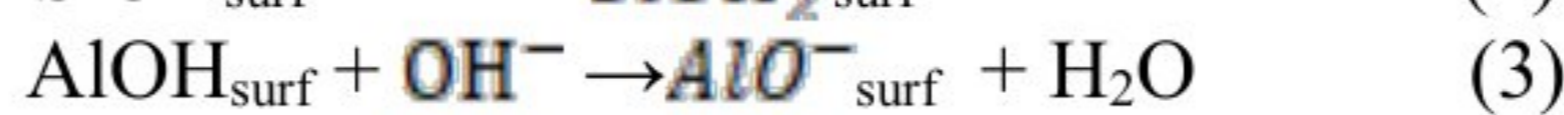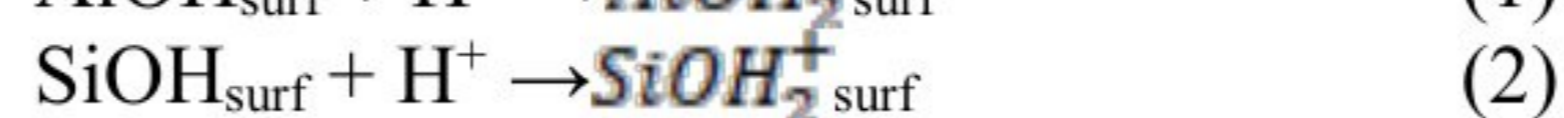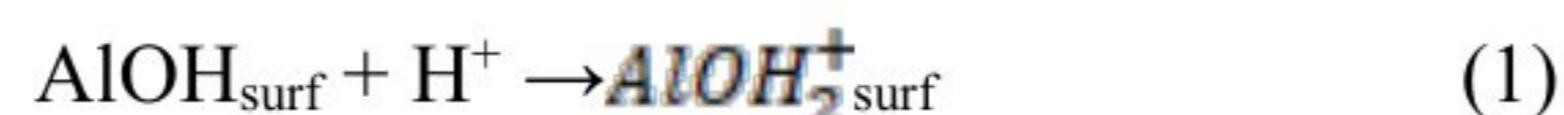
1) C 460; 2) N 100; 3) A 120; (pH=7.8).

It can be seen that the highest settling rate was obtained in the presence of anionic flocculant A120 (Fig.2, curve 3). A sharp increase in the settling rate was observed from 9 to 25 m / h with an increase in the concentration of A120 from 40 to 100 g /t. Settling of large flocs was intensive in the first two minutes and stoped within ten minutes. The resulting supernatant was without colourless, with the transparency about 98%. Further rise in A120 concentration had not any significant effect on the settling rate.

The wastewater settling tests, in which the inorganic coagulant $Al_2(SO_4)_3$ was only used in concentration from 0.4 to 4 kg/t, demonstrated almost identical settling with the natural one. The use of 0.4 to 1.2 kg/t $Al_2(SO_4)_3$ in combination with the most efficient flocculant A120 (100 g/t) gave similar results to those when only A120 was used in the same concentration. High coagulant concentrations added and 100 g/t of A120 g/t gave lower settling rate and turbid zone above the deposit.

A notable result was obtained when, instead of inorganic coagulant $Al_2(SO_4)_3$, cationic flocculant C581 (polyamine), was used with A120, in the concentrations of 40 g/t C581 and 100 g/t A120 (Fig.3., curve 3). The settling rate was slightly higher than with A120 alone, in the mentioned concentration (curve 2).

However, flocs were large, settling very intensive in the initial ten seconds and practically completed within three minutes. Supernatant transparency was about 99%.

It is well known that the surface charge on the aluminosilicates when suspended in aqueous medium is pH-dependent because of protonation and deprotonation reactions involving H^+ and OH^- ions. The sites that may be present on the clay surface are the following: aluminol group, $AlOH_{surf}$, and silanol group, $SiOH_{surf}$ [4]. But, due to the protonation and deprotonation reactions on the clays suspended in an aqueous medium the next surface centres can be formed:

$$AlOH_{surf} + H^+ \rightarrow AlOH_2^+{}_{surf} \qquad (1)$$
$$SiOH_{surf} + H^+ \rightarrow SiOH_2^+{}_{surf} \qquad (2)$$
$$AlOH_{surf} + OH^- \rightarrow AlO^-{}_{surf} + H_2O \qquad (3)$$
$$SiOH_{surf} + OH^- \rightarrow SiO^-{}_{surf} + H_2O \qquad (4)$$

Protonation/deprotonation reactions of $SiOH_{surf}$ group (reactions 2 and 4) also determine the surface charge of the quartz particles.
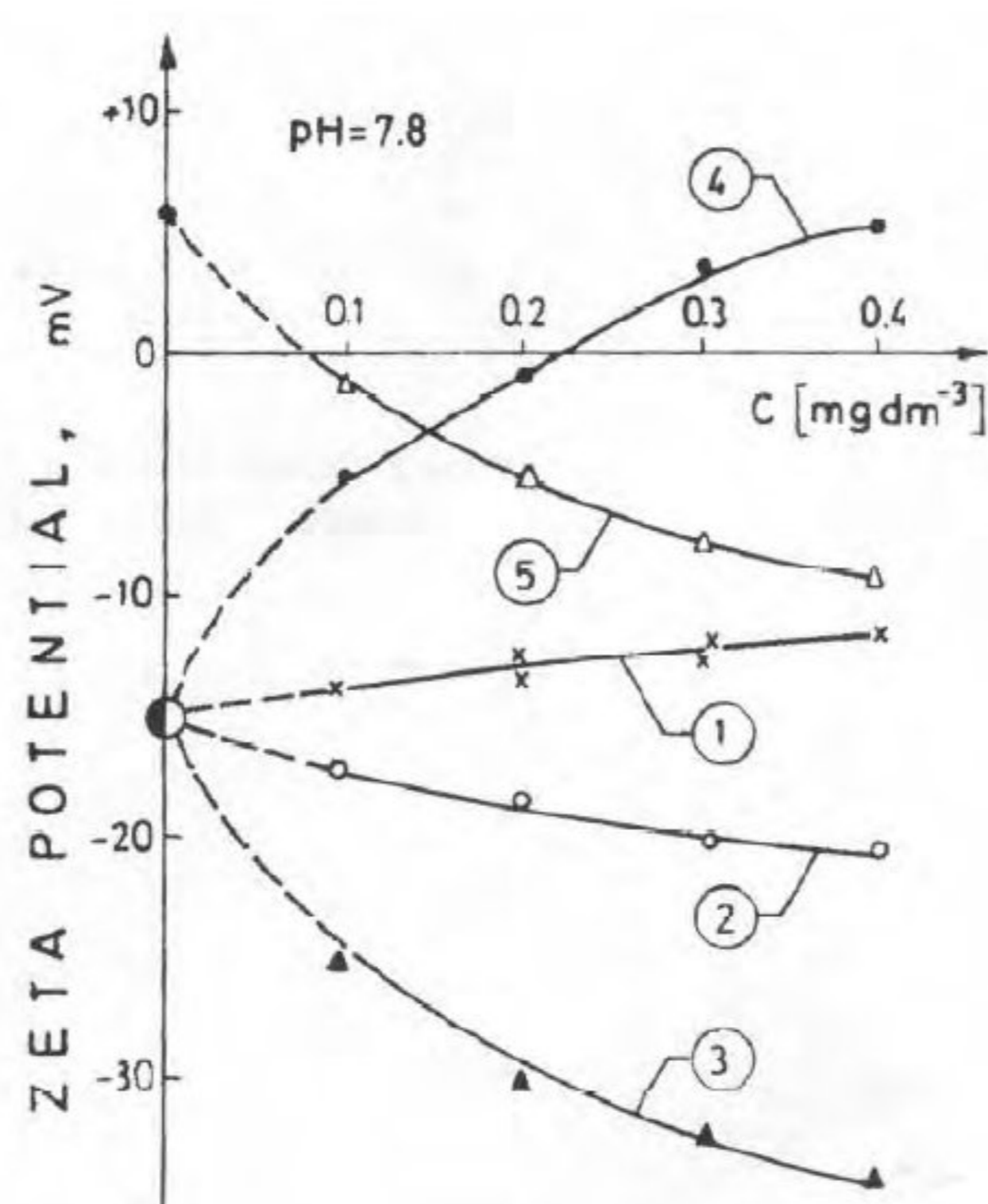
Zeta potential of dispergated particles in clayed wastewater has negative value (-15 mV) in the absence of any flocculant (Fig.4). It means that the relative ratio of numbers of negative/positive surface sites (Θ^-/Θ^+), i.e. the relative ratio of surface densities of negative/positive surface sites which are formed at pH 7.8, is higher than 1.

But surface negative centres have very low affinity for C460 cations, which was confirmed by settling test (Fig.2, curve 1), as well as by zeta potential data (Fig.4, curve 1).

The adsorption of nonionic N100macromolecules probably occurs on $Al\text{-}O^{\delta-}\text{-}H^{\delta+}{}_{surf}$ or $Si\text{-}O^{\delta-}\text{-}H^{\delta+}{}_{surf}$ centres due to the formation the hydrogen bond between the electronegative atoms, N or O from N100 molecule and hydrogen from aluminol or silanol groups. Weak rise of negative zeta potential values (Fig.4, curve 2) is resulted by occupations of marked positive surface sites with N100 macromolecules, giving the rise in the relative Θ^-/Θ^+ ratio.
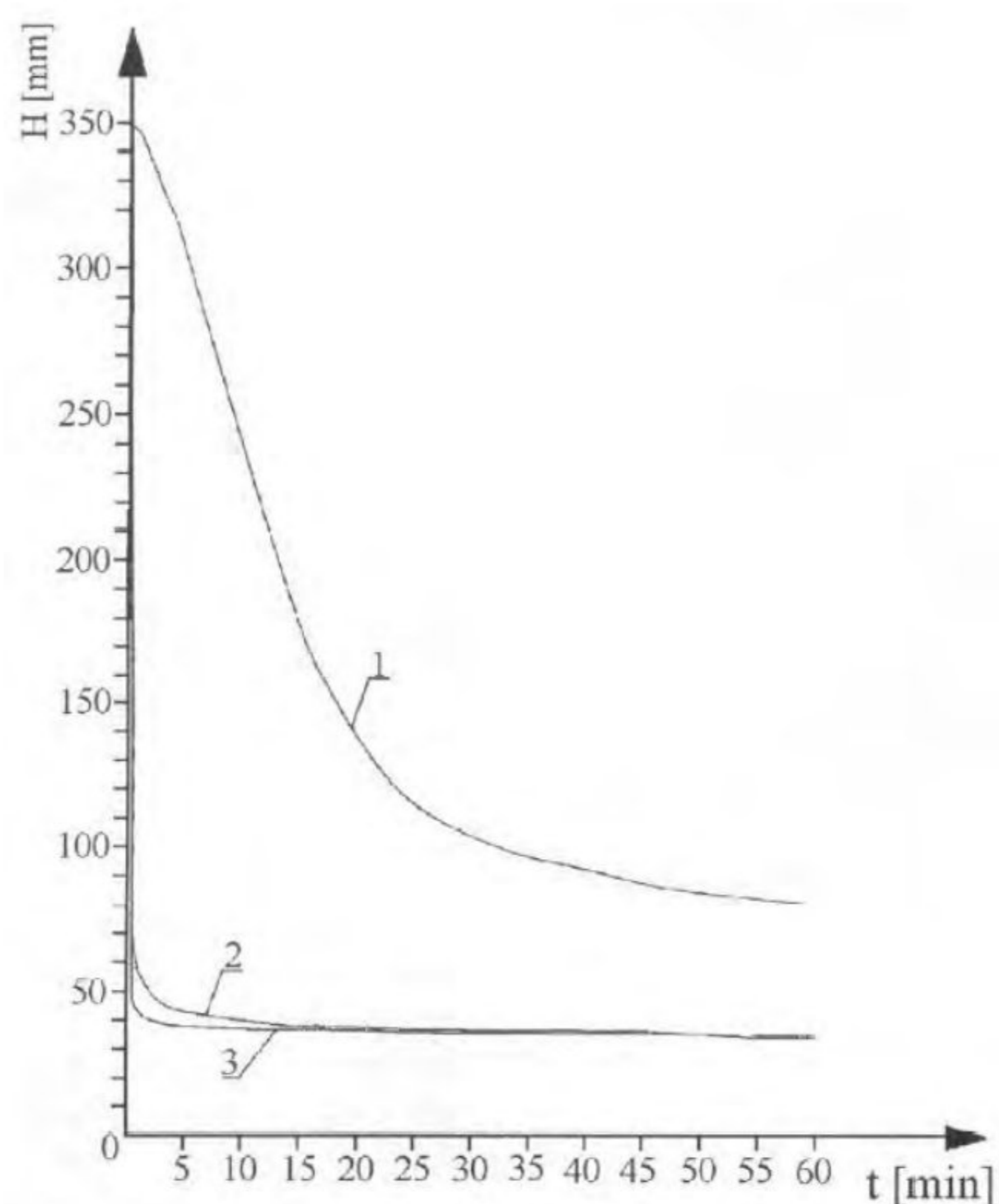
Figure 3. *Sedimentation curves of clayed wastewater in the in the presence of: 1) without flocculant; 2) 100g/t A120; 3) 40 g/t C581 and 100 g/t A120.*

Figure 4. Zeta potential of the dispergated particles in clayed wastewater as a function of a flocculant concentration:1) C460; 2) N100; 3) A120; 4) C581; 5) C581 (0.4 mg dm^{-3}) and A120.

The best flocculation result can be explained by the highest affinity of surface positive sites for anionic flocculant A120. The chemical adsorption of A120 anions on $AlOH_2^+{}_{surf}$ or $SiOH_2^+{}_{surf}$ sites and the electrostatic interaction on Al-O$^{\delta-}$-H$^{\delta+}{}_{surf}$ or Si-O$^{\delta-}$-H$^{\delta+}{}_{surf}$ centres are confirmed by the rise in the negative zeta potential values (Fig.4, curve 3). But, the high settling rate and large flocs indicate that A120 anions have more active negative sites and bridge more dispergated particles. The means that the dominant mechanism of flocculation in the presence of A120 is bridging of particles.

The cationic flocculant C581 was obviously adsorbed on some negative surface sites $(AlO^-{}_{surf}$ or $SiO^-{}_{surf})$ of disperged particles (curve 4) better than Al^{3+} or Al-hydroxycations, giving more positive surface centres for the adsorption of A120 anions (curve 5). On this way C581 reduced the double layer repulsion between the particles and attributed to the higher effectiveness of anionic flocculant A120 in heterocoagulation(flocculation of all the present particles in clayed suspension.

4. CONCLUSION

The effectiveness of flocculants used in purification of clayed wastewater was:

A120>>N100>>C460.

The chemical adsorption of A120 anions on $AlOH_2^+{}_{surf}$ or $SiOH_2^+{}_{surf}$ and their electrostatic interaction with Al-O$^{\delta-}$-H$^{\delta+}{}_{surf}$ or Si-O$^{\delta-}$-H$^{\delta+}{}_{surf}$ sites of dispergated particles occur. Using A120 the polymer bridging is the dominant mechanism of flocculation in clayed wastewater. The settling rate was about 25m/hr in the presence of 100 g/t A120. The resulting supernatant was colourless and had 98% of transparency. A similar settling rate was obtained using the combination of C581 and A120, but the time of the end of sedimentation was shorter (3 minutes). C581 cations are probably adsorbed on negative particle sites $(AlO^-{}_{surf}$ or $SiO^-{}_{surf})$, reducing the double layer repulsion between the particles and contributing to the effectiveness of A120, i.e. to heterocoagulation/flocculation of all the dispergated mineral particles.

The electrokinetic behavior of the particles in clayed wastewater in the presence of used reagents suggests that the bridging is dominant mechanism of flocculation, although charge neutralization contributes in the reduction of the double layer repulsion and better adsorption of some flocculant ions on dispergated particle surface.

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