Coagulation considerations – possible and real processes

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Abstract
On the basis of laboratory experiments, other available information and theoretical considerations, the possible coagulation mechanisms were investigated and the real processes were determined in relatively high alkalinity surface waters. It has been verified that water soluble compounds of coagulants, such as aluminium- and ferric ions, and their water soluble hydrolysis products (hydroxide polymers) do not play important role in destabilisation of colloid, quasi-colloid particles. The stability ("life time") of these components is low; consequently their transformation occurred within a very short time. The main reason of the quick transformation is the high alkalinity of surface water. The high alkalinity provides the possibility for fast hydrolysis and precipitation of the metal ions of coagulants (Al^{3+}, Fe^{3+}), and water soluble hydroxide polymers, respectively. The metal ions of coagulants transform into weakly water soluble compounds within some seconds after the coagulant feeding. The most stable compound is the positively charged aluminium- and ferric hydroxide sol, but after their appearance intensive aggregation starts immediately. Although the probability of sol-sol aggregation is much higher than sol adsorption onto the particle surface, this latter process provides the destabilisation of colloid, quasi-colloid systems. The rates of the main processes are extremely quick, and the application of intensive and rapid mixing is recommended.
Keywords: Adsorption, coagulant, colloid destabilisation, high alkalinity, hydrolysis

INTRODUCTION AND SHORT REVIEW

One of the crucial unit operations in the treatment of surface waters is clarification, which comprises the processes of coagulation, flocculation and subsequent sedimentation or flotation. The solid particles forming colloidal, quasi-colloidal dispersions in water are transformed by the coagulation, flocculation processes into forms suited to being removed from the water by simple solid-liquid phase separation techniques - including also filtration after sedimentation. Effective filtration requires powerful coagulation of suspended solid particles of surface waters. Some of the dissolved organics present in the water combine with the hydrolysing coagulant and become thus also accessible to such solid-liquid phase separation methods.

The efficiency of coagulation-flocculation processes in the treatment of surface waters depends primarily on the type and rate of the reactions combining the colloidal particles and the dissolved organics with the coagulant (Al^{3+} or Fe^{3+} ions and their hydrolysis products), further on the strength and durability of the ensuing bonds.

Relying on the theory developed and applied successfully for destabilizing and coagulating colloidal sols towards the end of the last century, the Al^{3+} and Fe^{3+} ions were believed responsible - according to the Schulze-Hardy rule - for coagulating and flocculating the suspended fines at water works treating surface water with aluminium and iron(III) salts. In the first half of the 20th century the experiments and measurements of Mattson called attention to the fact that coagulation of the suspended solids in surface waters was attributed mainly to the hydrolysis products of the ions mentioned above, the aluminium and iron(III) hydroxides (Mattson, 1928).

According to Gregory (1979), under particular conditions both the aluminium ions, the $[Al_4(OH)_8]^{4+}$ complexes (specific adsorption) and the $Al(OH)_3$ compounds (sweep coagulation) can play a controlling role in coagulating the colloidal, quasi-colloidal dispersion. The ratio of the abovementioned processes depends on the amount of aluminium salt added, on pH and on the concentration of the suspended solids.

Parthasarathy and Buffle (1985) succeeded in demonstrating experimentally that within a wide (4.0 - 6.5) range of pH values and Al concentrations (10^{-3} - 10^{-1} mol/L) and at OH - Al ratios between 2.5 - 2.9 : 1, over 75% of all the aluminium present is a water soluble complex $[Al_{13}(OH)_{32}]^{7+}$. The chain length of this complex is 0.1 - 0.2 nm, and is thus smaller by several orders of magnitude than the suspended solids to be removed. The authors claimed this polymer, in which the positive charge per Al atom varies from 0.53 to 0.56, to be a highly effective coagulant.

The formation of water soluble metal-hydroxide species and their adsorption onto the surface of particles take place extremely quickly, within microseconds for monomeric species and within 1 s if polymeric species are involved (Hahn and Stumm, 1968). The formation of the aluminium or ferric hydroxides for entrapment of colloidal particles is completed within the range of 1 to 7 s (Letterman et al, 1973). Since the hydrolysis reaction and the adsorption of hydrolysis products onto the particle surface are fast and essentially irreversible, a complete distribution of the hydrolysing aluminium and iron(III) salt in less than 0.1 s is required (Klute, 1990).

The aims of this paper to investigate the possible coagulation mechanisms in high alkalinity (>1,5 mmol/L) surface waters and to determine the real processes on the basis of own laboratory experiments other available information and theoretical considerations.

MATERIALS AND METHODS

Aluminium- and iron(III) salts were added as coagulants to samples taken from different surface waters in Hungary (pH=6.8-8.4, HCO_3^-=0.8-4.5 meq/L) and to model systems created by dissolving in distilled water Ca^{2+}, Mg^{2+} and HCO_3^- ions in known proportions. The changes in the stability of the colloidal, quasi-colloidal dispersion was determined, settling of the flocs developed and the conversion of the three-valent metal ions of the coagulant into metal hydroxides were taken place.

The pH was adjusted when found necessary by adding sulphuric acid or sodium hydroxide. In some experiments a colloid stabilizing organic substance (sulphite liquor from a cellulose mill) was also added. In several experiments the sequence of adding the coagulant and the colloid stabilizing substance, and that of adding the coagulant and the suspended solids was reversed.

The experimental results were evaluated in terms of the measured changes in the zeta-potential, turbidity, pH alkalinity and the concentration of the dissolved coagulant. The dissolved and solid substances were separated by passing the sample through an 0.45 μm pore-size membrane filter. The zeta potential was measured by means of a Riddick-type ZETA METER, turbidity by a spectrophotometer, while for measuring the metal (Al, Fe) concentration of the coagulant and the products thereof a PERKIN ELMER atom absorption spectrophotometer was used.

Simple calculation were performed to estimate the ratio of the number of aluminium and ferric ions, and number of suspended particles, hydrogen-carbonate ions etc. On the basis of these estimations the probability of stability ("life time") of different compounds, originated from dissolved coagulants were determined.

RESULTS AND DISCUSSION

Calculation the probability of adsorption and hydrolysis of aluminium- and ferric ions

Metal ions (Al^{3+}, Fe^{3+}) of coagulants, feeding into surface waters, should perform two simultaneous, competitive processes, when the alkalinity of water high enough (>1.5 mmol/L):

- aluminium- and ferric ions, having high specific positive charge, adsorb onto surface of particles the colloid, quasi-colloid dispersion, changing their high negative electric charge
- aluminium- and ferric ions hydrolyse, forming positively charged water soluble metal hydroxide polymers are containing different, but maximum some dozen Al or Fe atoms

The probability of abovementioned two processes taking place was studied, when the suspended solids concentration was 100 mg/L, the average particle diameter 1.0 μm, the average density of particles 1.4 g/cm^3, the alkalinity 1.5 mmol/L and Al^{3+} dose 0.2 mmol/L. During the hydrolysis 1 mmol Al^{3+} products 3 mmol H^+ which react the HCO_3^- ions, reducing the alkalinity of water.

Table 1. Ratios of ions and particles

Material	Concentration	No. of particles, ions	Ratios
Suspended solids (ss)	100 mg/L	$1.37*10^{11}$	$HCO_3^-/ss = 6.6*10^9$
HCO_3^-	1.5 mmol/L	$6.03*10^{23}*1.5*10^{-3}$	
Al^{3+} (dosing into water)	0.2 mmol/L	$1.2*10^{20}$	$Al^{3+}/ss = 0.88*10^9$
H^+ (form during hydrolysis)	0.6 mmol/L	$3.6.0*10^{20}$	$HCO_3^-/H^+ = 2.5$

One of the most important conditions the Al^{3+} and Fe^{3+} ions hydrolysis is the fast reaction of H^+ and HCO_3^- ions. Considering the data of Table 1 it is proved that the probability of frequent collision of H^+ and HCO_3^- ions is high (near to 0.5) but the probability of collision of Al^{3+} ions and suspended particles is much more less, the order of magnitude is 10^{-9}. Consequently, the hydrolysis is the significant process, and the adsorption of Al^{3+} ions onto the surface of suspended particles does not have important role in the destabilisation of colloid, quasi-colloid dispersion.

Calculation of possible probabilities of adsorption and precipitation of positively charged water soluble aluminium- and ferric hydroxide polymers

During the hydrolysis of aluminium- and ferric ions the positively charged, water soluble hydroxide polymers are formed. The polymer hydroxides contain some aluminium or iron atoms, but their maximum number is restricted, not higher than some dozen. The water soluble aluminium and ferric hydroxide polymers participate in two simultaneous and competitive processes, which are as follows:

- metal (Al and Fe) hydroxide polymers adsorb onto the surface of colloid, quasi-colloid particles decreasing their high negative electric charge
- precipitation of water soluble aluminium- and ferric hydroxide polymers

The possible probability of these two processes is evaluated on the basis of the data Table 2.

Table 2. Ratios of ions, hydroxide polymers and particles

Material	Concentration	No. of particles, ions, hydroxide polymers	Ratios
Suspended solids (ss)	100 mg/L	$1.37*10^{11}$	$HCO_3^-/ss = 3.52*10^9$
HCO_3^-	0.7-0.9 mmol/L	$6.03*10^{23}*0.8*10^{-3}$	hydroxide polymers/HCO_3^-= $2.61*10^{-3}$
Al-hydroxide polymers (supposed average No. of Al atoms = 100	near to 0.2 mmol/L but less	$1.26*10^{18}$	hydroxide polymers/ss = $9.2*10^6$

Supposing that near to all aluminium ions hydrolyse, and the average number of Al atoms in one hydroxide polymer is 100, $1.26*10^{18}$ individual water soluble aluminium-hydroxide polymer appear in one litre. The precipitation of soluble hydroxides should occur along two pathway:

- further hydrolysis, depending on HCO_3^- concentration
- frequent and effective collisions of polymer molecules

Data of Table 2 demonstrate that the probability of the water soluble hydroxide polymers is extremely low (10^{-7}), but the possibility of further hydrolysis (to get the "total hydrolysis" i.e. ratio of –OH and Al atoms is 2.8-2.9/1), and the number of effective collisions are much higher (10^{-3}, 0.5, respectively). In the '70s and '80s it was verified by different experiments that the aluminium and ferric-hydroxides formed during hydrolysis of coagulants, are able to change the negative electric charge of colloid, quasi-colloid particles within very short time (Amirtharajah and Mills 1982, Hahn and Stumm 1968, Klute, 1990, Latterman et al. 1973, Licsko, 1976). Amirtharajah and Mills (1982) reported that the hydrolysis products developed in the time range 0.01 – 1.0 s, following the coagulants feeding, caused the most effective destabilisation of colloid, quasi-colloid system.

Our laboratory experiments have demonstrated that the precipitated aluminium-hydroxides appeared after the coagulant feed immediately. In the optimum pH range for aluminium-hydroxide precipitation (6.5-7.5) close to all Al^{3+} ions transformed into poorly water soluble components. It means that the "life time" of water soluble aluminium hydroxide polymers is extremely short, consequently these aluminium compounds should not have significant role in the destabilisation of disperse systems. This statement is valid, when the alkalinity of surface water is high enough (>1.5 mmol/L), the pH of treated water is situated in the range of 7.0 – 7.5 and the coagulant feeding is changed in the range of 0.15 – 0.35 mmol/L range.

Possibilities of sol-sol aggregation and sol adsorption onto the surface of suspended particles
As it has been stated, the Al^{3+} and Fe^{3+} ions of coagulant transform into poorly water soluble compounds during extremely short time. The precipitated hydrolysis products form colloid sols, which have positive electric charge. Although the electric charge of the hydroxide sols is the same, these sols are able to aggregate. The freshly formed aluminium- and ferric hydroxide sols participate in two simultaneous and competitive processes, which are as follows:

- positively charged hydroxide sols, in spite of that they have the same electric charge, within very short time, are able to aggregate each others and form flocs (gels) which accessible for solid-liquid phase separation (i.e. sedimentation, flotation, filtration - on traditional rapid sand filter).
- positively charged hydroxide sols adsorb onto the surface of colloid, quasi-colloid particles changing (decreasing) their high negative charge. Sol-particle complexes, having close to zero electric charge, aggregate with each other and the individual sols, forming flocs (gels) accessible for solid-liquid phase separation

Sol-sol aggregation is not advantageous process considering the destabilisation of colloid systems. Performing simple calculations it has been stated that sol-sol aggregation has higher probability than the sol adsorption onto the solid particles. It can be supposed that aggregation rate of positively charged sols does not so high than hydrolysis rate of aluminium- and ferric ions, or precipitation rate of water soluble hydroxide polymers. The most important reason of this reduced rate is the repulsing effect, originated from same electric charge. In spite of the abovementioned fact, the significant part (30-50%) of the sols aggregate within one second (Figure 1).

It was verified earlier by laboratory experiments that within one minute, after the coagulant feeding, the electric charge changing effect of freshly formed aluminium- and ferric sols has decreased

significantly (Licskó, 1991). Considering the quick floc growth, the relatively big flocs (theoretical diameter is bigger than 0.1 mm) are not able to change significantly the negative electric charge of suspended particles.

The basic and most effective process considering the negative electric charge changing of the colloid, quasi-colloid particles is the adsorption of positively charged sols onto the surface of particles. It is true that this process is not the dominant one, but the repulsing effect, existing among the sols, provides enough individual sol particles for adsorption and electric charge change of the suspended particles. Furthermore, the natural equilibrium, existing between the sol-sol aggregation and sol adsorption, can be changed. The sol-sol aggregation may decrease by intensive and rapid mixing of coagulant.
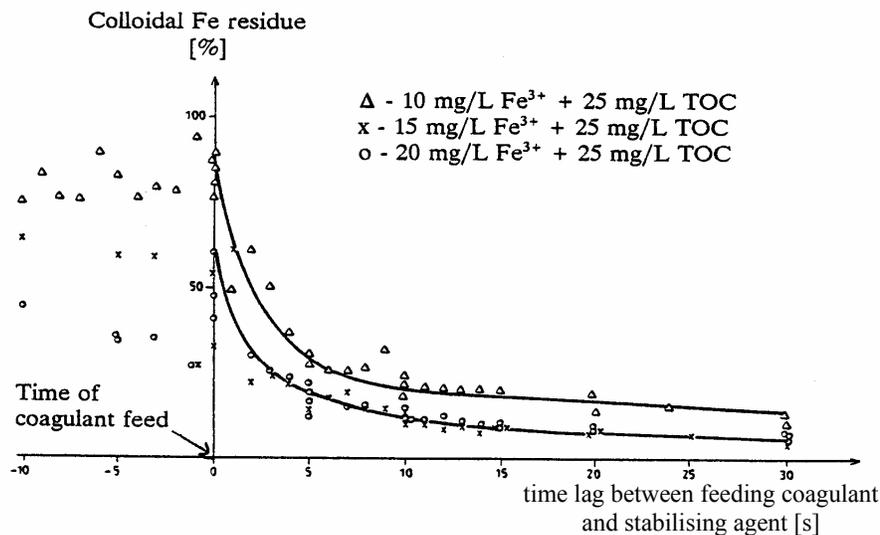

Figure 1. Precipitation of coagulant and floc growth

CONCLUSIONS
Coagulation processes, performed after the coagulant (Al^{3+}, Fe^{3+}) feeding into the surface waters were investigated and evaluated by laboratory experiments and simple calculations. It was determined that performing of possible coagulation mechanisms depends on the chemical characters of surface water, mainly on the pH value and hydrogen-carbonate concentration.

Inorganic coagulants, feeding into the surface waters, dissociate into their ions. The Al^{3+} and Fe^{3+} ions may adsorb onto the surface of particles, changing their high negative electric charge. Simultaneously these ions hydrolyse, if the alkalinity of water is high enough. The difference between the rates of these two simultaneous processes may be some magnitude, the reason is the relatively high (>1,5 meq/L) alkalinity of water. Aluminium- and ferric ions transform into positively charged water soluble aluminium- and ferric-hydroxides before they could get and adsorb onto the surface of colloid, quasi-colloid particles. Consequently, the adsorption of aluminium and ferric ions does not have significant role during decreasing the stability of colloid, quasi-colloid dispersion.

The "lifetime" of water soluble aluminium- and ferric hydroxide polymers is extremely short when the alkalinity of the water is so high that the pH value is situated between 6.5 and 7.5 following the total hydrolysis of coagulants. Two simultaneous and competitive processes (precipitation of water

soluble hydroxide polymers and their adsorption onto surface the colloid, quasi-colloid particles) are performed, but the rate of precipitation is much (some magnitude) higher. Consequently, adsorption of water soluble hydroxide polymers does not significant role in decreasing the stability of colloid, quasi-colloid dispersion.

Precipitated aluminium- and ferric hydroxides form positively charged sols. After the sol forming two simultaneous and competitive processes take place immediately: they aggregate with each others and adsorb onto the negatively charged particles. Although the aggregation of sols are hindered by their same (positive) electric charge, 5 seconds after the coagulant feeding the 75-85% of sols form flocs, with some dozen μm. These hydroxide flocs are able to decrease the stability of colloid, quasi-colloid dispersion very restrictly.

Although the probability of positively charged sols on the solid particles is much smaller than their aggregation, in the 0.15 – 0.35 mmol/L coagulant feeding range the number of adsorbed sols are enough for the necessary electric charge change i.e. to decrease the stability of colloid, quasi-colloid system.

Among the aluminium- and ferric ions and their hydrolysis products the poorly water soluble sols have better stability, i.e. their "lifetime" is longer. Consequently, positively charged sols have significant role in decreasing the stability of colloid, quasi-colloid system.

The aggregation of sols, which is an ineffective process considering the stability decreasing of colloid system, should delay by intensive, rapid mixing. The optimum of the rapid mixing is in the one – one and a half minutes range. The rapid mixing increase the hydrolysis rate of aluminium- and ferric ions and the adsorption rate of positively charged sols onto the surface of colloid, quasi-colloid particles.

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