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APPLICATION OF FERRONOMETRY IN DETERMINATION OF IN SITU AL SPECIES TRANSFORMATION IN PRE-HYDROLYZED COAGULANTS

ZASTOSOWANIE FERRONOMETRII W OCENIE TRANSFORMACJI IN SITU FORM GLINU W KOAGULANTACH WSTĘPNIE ZHYDROLIZOWANYCH

Wiarygodną metodą oceny skuteczności technologicznej koagulantów może być określenie udziału poszczególnych form glinu, które decydują o mechanizmach, a tym samym efektywności procesu uzdatniania. Jedną z metod, które pozwalają na charakterystykę powstających produktów hydrolizy jest metoda oparta na kolorymetrycznej reakcji hydrokompleksów glinu z feryonem. W oparciu o uzyskane wyniki stwierdzono, iż podczas reakcji strącania nierozpuszczalnych produktów hydrolizy koagulantów wstępnie zhydrolizowanych dochodzi do powstawania dużej ilości drobnych cząstek spowodowanych przemianą insitu form monomerowych w polimerowe. Cząstki te nie zawsze zostają przyłączone do większych agregatów. Dlatego też, bardzo istotne jest dokładne określenie dawki koagulantu w stosunku ilości zanieczyszczeń obecnych w wodzie. W przypadku, gdy te stosunki są nieodpowiednie mamy do czynienia z gwałtownym wzrostem liczby bardzo drobnych cząstek (<5 mikronów). Oznacza to, że również w przypadku stosowania koagulantów wstępnie zhydrolizowanych może dojść do ich przedozowania. W typowych warunkach najczęściej będzie się to objawiało wzrostem stężenia glinu w wodzie uzdatnionej, oznaczanego jednak dopiero przy użyciu innej metodyki niż powszechnie stosowanych metod spektrofotometrycznych.

1. Introduction

In WTP one of the most popular methods applied to improve treatment effectiveness is the change of a coagulant type. Pre-hydrolyzed coagulants have become more popular for their better contaminants removal than traditional hydrolyzing salts. The hydrolysis degree of polymeric Al coagulants can be controlled during manufacture. However, the complex nature of hydrolysis influences on formation of hydrolysis species. The hy-

drololysis effects depend on many factors: aluminium concentration, sort of adopted bases, methods of alkalization, co-existing anions and particles. Polyaluminum chloride (PACl) is one of the most important pre-hydrolyzed coagulants. PACl is less sensitive to changes in pH and temperature. Its high positive charge of some polycations is highly effective in neutralizing the negative charges of colloidal particles. Therefore pre-hydrolyzed coagulants are more effective in mineral particles removal than alum. However, it is not so obvious for coloured waters containing dissolved organic matter (DOM). Some researchers found that PACl precipitated fulvic acids (FA) over a broad pH range and could be a better reagent than alum, but on the other hand some investigators observed that PACl did not reduce DOM as effectively as alum. It mainly results from the complexity of DOM, what makes difficult to determine coagulation mechanisms, and from the variety of PACl products. Shi (2007) revealed in the study that when large molecular and hydrophobic humic acid was treated, the coagulation efficiency of preformed Al species (Al_{13} and colloidal species) was much less than that of conventional Al salt. The flocs formed by preformed Al species were smaller than those formed by conventional Al salt.

Pre-hydrolyzed coagulants are usually characterized by their basicity. However, the choice of a proper commercial reagent should be preceded by testing, because the basicity is not the reliable parameter in evaluation of treatment effectiveness. More useful method to evaluate these coagulants is aluminium speciation. Pre-hydrolyzed reagents are usually added to the source water without dilution and pre-treatment. After reagent dosing into water, it is diluted, and it undergoes a serial of hydrolysis, polymerization, aggregation and precipitation processes, which result in various metastable and transient species existing in bulk solution. Pre-formed polymer species are regarded to be stable what enables contaminants charge neutralization before Al precipitates. However, after a coagulant dosing into water, monomeric species undergo transformation to polymer forms. There is a significant difference between the stability of the pre-formed polymers and these formed in-situ. In-situ polymeric species rapidly transform into Al precipitates. Transformation of PACls species after dosing depends largely on the original composition. Low - polymerized PACls i.e. with the high amount of monomers show a significant change of species under various conditions [8]. The highest amount of polymers is formed at pH 6 [10]. Therefore at that pH value the most decrease of UV_{254} absorbance occurs. The increase of pH results in the decrease of polymer fraction. Hence, it may be expected that in the slightly acidic pH region, for good contaminants removal, PACl with low OH/Al ratio (B) should be employed, because transformation of monomers into polymeric species is the most effective. At basic pH, PACls with high value B removes UV_{254} absorbance more efficiently, because the amount of polymeric species is quite stable. For high B PACls, polymeric forms produced in-situ have no important influence on coagulation efficiency.

The objective of this work was to get more understanding on coagulation mechanisms of PACls of various polymerization degree. In the studies transformations of Al species after coagulant dosing into treated water were analyzed. The influence of pre-hydrolyzed coagulants doses were also considered. So far PACls were thought to be resistant to overdosing. The results of this work show that even pre-hydrolyzed coagulants can be overdosed. However, overdosing cannot be noticed on the base of standard analytical procedures. To find it out the measurements of particles number should be applied. It may be also confirmed by the measurement of total aluminium in water after treatment.

2. Materials and methods

2.1. Methods

The study was divided into two separate parts. The objective of the first part was to analyze the changes of particles size distribution (PSD) after coagulant dosing into tap water. In this study PACls at the doses: 1, 2, 3, 4 mgAl/L were tested. After rapid mixing (270 rpm, 10 s) PSD was determined (the analyzer IPS LCW Kamika Instruments). Particles size distribution was measured in the range $0,5 \div 30 \mu\text{m}$. The analysis was made at the first stage of flocculation. The data were collected after 90, 210, 330, 450, 570, 690 s flocculation time.

2.2. Determination of aluminium speciation by Al–ferron complexation timed spectrophotometry

Al species distribution was examined with ferron timed spectrophotometric “modified” method [3]. The applied procedure is a modification of the traditional method which is based on the different reaction time of aluminium species with ferron reagent (8-hydroxy-7-iodoquinoline-5-sulphonic acid) to form water soluble complexes in pH 5.0–5.2 [6]. These complexes can absorb light with a maximum at 370 nm. Absorbance measurements at this wavelength may allow the calculation of the different species of aluminium. A UV–vis spectrophotometer was used for this purpose. The rate constants of the ferron reaction with aluminium present in the form of monomeric, dimeric, tridecameric and polymeric complexes are respectively, ~ 2.3 ; ~ 0.97 ; $\sim 7.5 \times 10^{-2}$ and $\sim 3.1 \times 10^{-3} \text{ min}^{-1}$. It means that they are higher, the lower degree of polymerization. So, this method is based on kinetic analysis of the formation of the ferron–aluminium complex. It is stated that ferron reacts almost immediately (within 1 min) with the monomeric Al species (Al_a), while the intermediate polymeric structures of aluminium can react slower, i.e. at 120 min (Al_b). The absorbance at 120 min is attributed mainly to Al_{13} in the aluminium pre-polymerized coagulants, especially when high OH/Al molar ratio was applied. Finally, the even larger and rather insoluble polymeric structures, corresponding mainly to $\text{Al}(\text{OH})_3$ need much more time to react, or they would not react at all and their amount can be calculated from the subtraction of the two other aluminium species from the total aluminium concentration (Al_c). However, the authors [3] proved that the “classical” ferronometry cannot be applied for high pre-polymerized coagulants, because the reaction time with ferron is longer than 2 hours and results from the presence of high-polymerized species. So, in the “modified” ferronometry which was applied in this study, the end of the reaction was considered to be the achievement of a maximal absorption, which showed no further change. In this method Al_b species were described as quick-reacting (Al_{b1}) and slow-reacting (Al_{b2}) with ferron [1, 5 – 10].

2.3. Reagents

The investigation involved the study of three pre-hydrolyzed coagulants: PAC11, PAC12, PAC13. The characteristics of the coagulants is performed in Table 1. Table 2 presents aluminium speciation of coagulants determined by “modified” ferronometry.

Tab. 1. Characteristics of tested coagulants

Tab. 1. Skrócona charakterystyka testowanych koagulantów

Parameter	coagulant		
	PAC11	PAC12	PAC13
pH	3,94	4,21	3,5
Al [%]	9,32	11,46	12,5
basicity [%]	85,69	77,81	85,0

Tab. 2. Al species distribution of coagulants determined by „modified” ferronometry [3, 9]

Tab. 2. Analiza specjacyjna form glinu testowanych koagulantów określona w oparciu o “zmodyfikowaną” metodę ferronometryczną [3,9]

Al form [%]	coagulant		
	PAC11	PAC12	PAC13
Al ₁ *	12,6	2,3	40,8
Al ₂ *	36,7	10,2	59,2
Al ₃ *	50,6	87,5	0

*Al₁ – monomeric Al species determined within the first 60 – 70 seconds. In „classical” ferronometry they are described as Al_a

*Al₂ – low-polymerized Al species in the form of dimers and trimers. In „classical” ferronometry they are described as Al_{b1} (quick-reacting with ferron)

*Al₃ – average and high-polymerized Al species in the form of tridecameric and oligomeric complexes. In “classical” ferronometry they are described as Al_{b2} (slow-reacting with ferron) and Al_c (aluminium species in precipitated and colloidal complexes) if the reaction time is longer than 2 hours

3. Results and discussion

Figures 1-3 show the particles size distribution changes after coagulants introduction into water samples. The first data collected after 90 s reaction time show the significant increase of particles number in the range 0,5 do 30 μm in comparison to the amount noted in the water sample before reagent addition (approx. 200 particles). The longer reaction time the amount of particles of the analyzed size decreased independently of the coagulant type. At the beginning of the process the largest aggregates are generated when PAC13 is applied. This coagulant is the one out of all the tested coagulants which

is characterised by the lowest polymerisation degree (41% of monomers). The smallest aggregates are noted for PAC11. This reagent is produced in 'sulfate' modification and consists of 13% monomeric Al species. Hence, it is concluded that polymerization degree of tested reagents is not the factor which decides about the particles size. If the primary aluminium speciation was the decisive factor, the aggregates of the biggest size would be produced for PAC12 samples. It may result from the process of transformation of monomer forms (the highest amount of monomers were measured for PAC13) into polymers. The literature data show that the polymeric species produced in situ are much more effective in contaminants removal than primary polymers.

To explain the results presented above it is necessary to determine how much Al species is converted into polymeric species and to what extend the residual monomers may deteriorate the course of coagulation. So that to determine the influence of aluminium species transformations on particles size distribution and kinetics of the process, the ferron method was used. The Al species classification based on complex reaction kinetic of hydrolysis precipitates and ferron reagent show that the amount of polymeric Al forms distinctly increases when the coagulant is diluted with synthetic water before measurement. The increase depends on coagulant basicity. The most significant decrease of monomers (more than twice) in comparison to the samples without coagulant dilution is observed for PAC12 of basicity c.78%. However, taking into consideration the primary PAC12 speciation, i.e. only 2,3% of monomeric species, the above mentioned conversion is not important from the point of view of the new speciation characteristics. For the other reagents of basicity 85%, the amount of polymers and precipitates increased by 10%. Because of high pre-polymerization degree of PAC11 and PAC12, polymeric species produced in situ have no crucial influence on coagulation effectiveness. It is important when PAC13 is considered because this reagent is characterized by high amount of monomeric forms (40,8%).

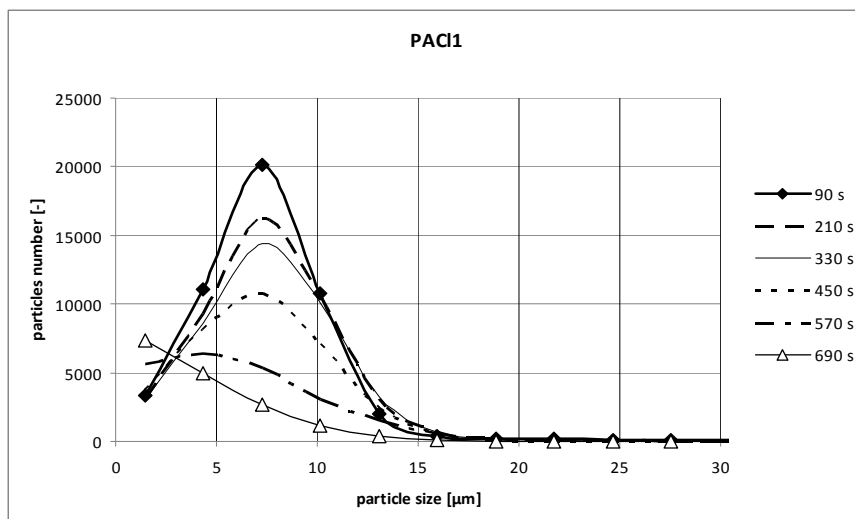


Fig. 1. Particle size distribution changes during coagulation with PAC11

Rys. 1. Zmiany rozkładu wielkości cząstek podczas koagulacji PAC11

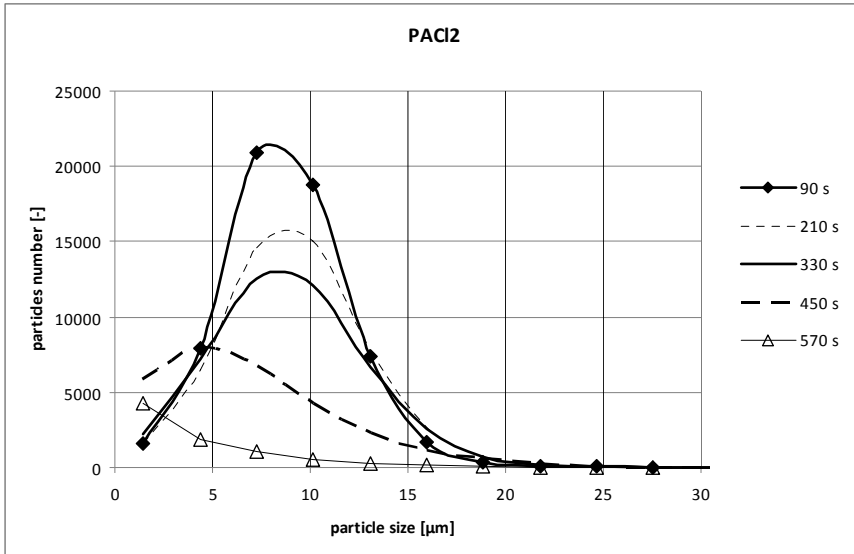


Fig. 2. Particle size distribution changes during coagulation with PAC12

Rys. 2. Zmiany rozkładu wielkości cząstek podczas koagulacji PAC12

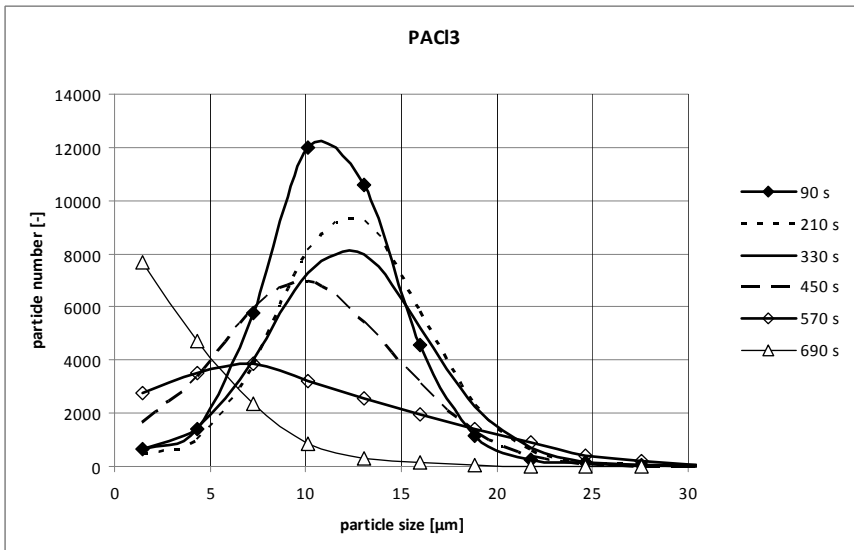


Fig. 3. Particle size distribution changes during coagulation with PAC13

Rys. 3. Zmiany rozkładu wielkości cząstek podczas koagulacji PAC13

Figure 4 presents changes of particle size distribution under conditions of PAC12 overdosing. It is observed that, in comparison to the source water, in the final phase of testing after coagulants application the amount of particles of very small size ($<5 \mu\text{m}$) increased.

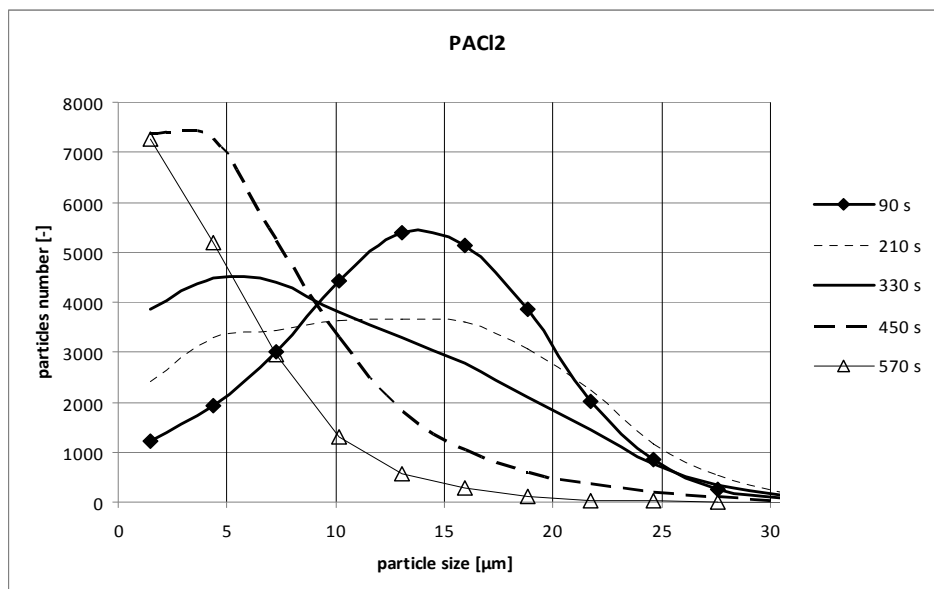


Fig. 4. Particle size distribution changes under conditions of PAC12 overdosing

Rys. 4. Zmiany rozkładu wielkości cząstek w warunkach przedawkowania PAC12

The similar observations were obtained during the research on coagulant dose optimization with the application of the particle counter [2]. The results of that research have indicated that for hydrolyzing coagulants only one extreme of function, which describes the relationship between coagulant dose and particles number, is found. In case of pre-hydrolyzed coagulants more than one extreme is noted. Such variations of particles concentration may be caused by changes of the source water quality or by breakage of post-coagulation aggregates or by the presence of coagulant precipitates of very small size which amount depends on a reagent dose. So, it was necessary to find the answer to the question what is the source of these small particles. In the study of Yan and Wang (2008) the floc was divided into three categories:

1. precipitated floc, which could settle down in the jar test apparatus at experiment condition,
2. colloidal floc, which cannot settle down in the jar test apparatus, but it can be filtered off by filtration through $0.45 \mu\text{m}$ filtration membrane,
3. NOM–Al floc, which is not large enough to be removed by filtration through $0.45 \mu\text{m}$ filtration membrane.

The purpose of coagulation is to get aggregates of the first group and to minimize the number of particles of groups 2 and 3 or their agglomeration with larger flocs. Therefore,

to determine the conditions of the analyzed process it was necessary to establish the form of small particles which were observed in figure 4. The additional ferronometry measurements were made. The coagulants were diluted by synthetic water and after 720 s they were filtered by 0,45 μm membrane filter and then tested using Al–ferron complex colorimetry according to the stated method. As shown in figure 5 reaction kinetics for PACI3 in filtered samples is different from the unfiltered samples. In filtered samples since the 6 -7th minute of measurement the reaction rate did not change, then suddenly decreased and it was followed by the slow increase. This means that particles which were removed during filtration were of polymeric form. Residual monomeric species converted into more complex form but with some delay (since 400-500s from the moment when the measurement started). This indicates that the increase of the amount of small size particles observed in fig. 4 is connected with the precipitation of monomeric forms or their conversion into polymers. These forms are susceptible to agglomeration in sweep coagulation. The crucial factor is to determine a coagulant dose which prevents from colloids restabilization.

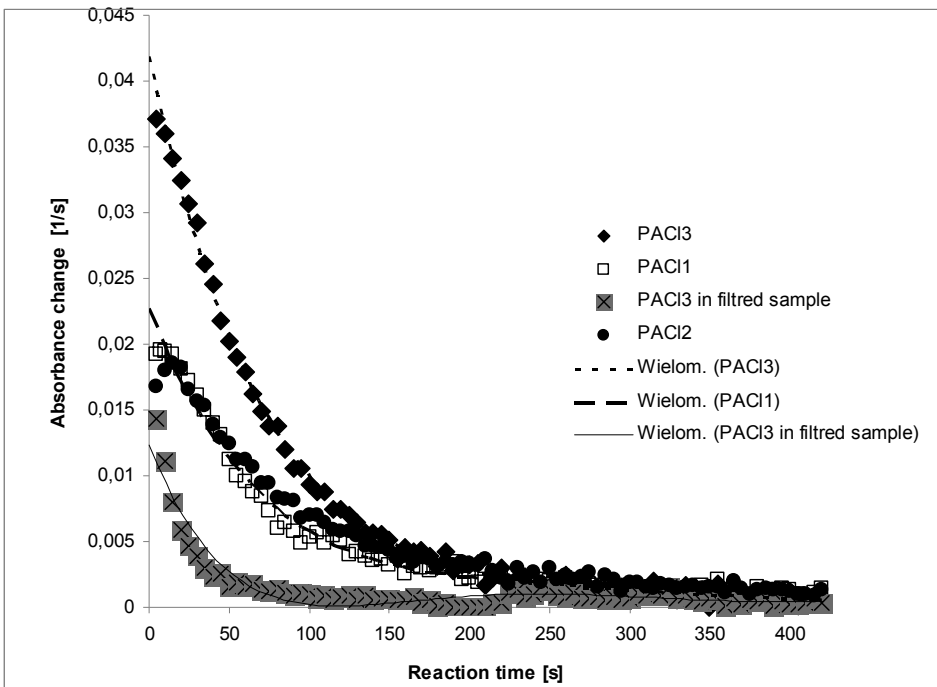


Fig. 5. Al–ferron analysis of the coagulants hydrolysis

Rys. 5. Analiza ferronometryczna hydrolyzy koagulantów

Figure 5 also presents the reaction rates for all tested coagulants in unfiltered samples. The analysis of absorption curves show that the reaction rate was the highest for PACI3 which is the lowest polymerized coagulant (41% of monomers). The kinetics reactions

for PAC11 and PAC12 are similar. Initially, the reaction rate for high-polymerized reagents (PAC11 and PAC12) significantly increases and then it starts to decrease. The discrepancies between the rates for high-polymerized coagulants and PAC13 are noted especially in the first phase of the reaction with ferron (30 seconds). If we assume that in this phase mainly monomeric forms react with ferron, the observed changes of reaction rates may be explained by precipitation of Al complexes. As it was proved in the previous research, Al precipitates can also react with ferron [3]. This means that the reaction rate between ferron and freshly produced precipitates is slower. Taking into consideration that monomers react with ferron at higher rate than with polymer forms, it was stated that this rate depends not only on primary coagulant basicity but first of all on primary monomeric forms concentration.

To sum up, it may be concluded that during precipitation of hydrolysis products of pre-hydrolyzed coagulants much amount of small particles ($\leq 0,5 \mu\text{m}$) is produced. It results from conversion in situ monomeric into polymeric forms. These particles are not always attached to larger aggregates and it may result from coagulant overdosing. That is why, it is very important to adjust the precise coagulant dose to the contaminants concentration in treated water. The coagulant overdosing usually causes the increase of residual aluminium in water after treatment, but it is crucial to make the measurement of total Al basing on the method different from the commonly used spectrophotometry. Such phenomenon was observed at the WTP (water treatment plant) where surface water contaminated with high amount of humic acids and turbidity is treated with a high-polymerized coagulant. Standard analyses of that water quality after treatment show that the process is effective and no abnormalities are observed. However, the analyses of residual total aluminium indicate that too high coagulant dose are periodically applied.

4. Conclusions

1. Polymerization degree of a coagulant is not the crucial factor which decides about size of aggregates produced in the first phase of flocculation. Polymeric species produced in situ seem to be much more decisive.
2. After coagulant dosing into water transformation of monomers starts. However, as far as treatment effectiveness is concerned, it is only significant when coagulation with low-polymerized coagulant (PAC13) takes place.
3. When pre-hydrolyzed coagulants are applied, during the process of precipitation of insoluble hydrolysis products, much amount of small particles is produced. The increase of such small particles is connected with formation of reaction products of precipitation of monomeric forms or their conversion into polymeric ones. These forms are susceptible to agglomeration in sweep coagulation. It means that for pre-hydrolyzed coagulants the commonly used procedures of coagulant dose optimization should be verified. Standard analyses of water quality are insufficient.

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