JOLANTA GUMIŃSKA*

PROCESS OF FLOCS AGEING AND ITS INFLUENCE
ON FLOCCULATION EFFECTIVENESS

The effectiveness of conventional coagulation depends first of all on the stability of flocs and their sorption ability. On the basis of the research results it was concluded that aluminium coagulant is hydrolysed independently of water temperature and this process is followed by precipitation of aluminium hydroxide flocs. However, in water of low temperature, as time goes by, the process of desorption and flocs disintegration starts, hence the process of coagulation is ineffective.

1. INTRODUCTION

Coagulation is the process of decreasing a colloid dispersity. RIDDICK and MOFFET [1] reported that in the first second after coagulant dosing chemical reactions are completed. At this moment hydroxides are generated and the process of destabilization of colloidal contaminants also takes place. From hydroxides and destabilizated colloids microflocs are produced. The above-mentioned processes are essential for coagulation and they control its effectiveness. LICSKO [2] claimed that in one minute hydroxide flocs lose their ability to destabilize the colloids and to coagulate raw water. This is due to the fact that hydroxide flocs cannot create a stable system with water contaminants. If freshly produced hydroxides do not meet water colloidal contaminats, e.g. because of insufficient mixing, they soon lose their ability to destabilize colloids and the process of their aggregation by hydrogen bonds takes place, i.e. the process of coagulation is not effective enough.

In the opinion of FRANÇOIS, Van HAUTE and WINDERICK [3], lenghtening of the flocculation time by over 30 minutes, i.e. a floc ageing, results in the decrease of its size. From the moment the flocs reach their maximum size, the process of irreversible changes in their structure begins. Based on the example of aluminium hydroxide FRANÇOIS and BEKAERT [4], [5] distinguish three mechanisms of flocs ageing. They as follows:

_____

* Silesian University of Technology, Faculty of Energy and Environmental Engineering, Institute of Water and Wastewater Engineering, Konarskiego 18, 44-100 Gliwice, Poland.

- aggregation–cementation,
- condensation–polymerization,
- crystallization.

In the first stage, the process of aggregation–cementation is greatly responsible for shrinking of flocs. During 6–8 hours, depending of flocculation conditions, a floc diameter decreases from 550 μm to 220 μm. For next four days, because of the condensation–polymerization and the crystallization processes, this diameter is reduced to 180 μm. In the third stage, a floc diameter increases due to crystal ripening (Oswald's law).

In their research, FRANÇOIS and BEKAERT [4] analysed parameters influencing the process of floc ageing. Their results prove that the amount of suspension and the time of quick mixing have the most important influence on the mechanism of cementation. Mixing energy and a coagulant dose are crucial parameters which affect the crystallization rate. The effect of pH value is surprisingly small. A coagulant dose, the amount of suspension and pH have a considerable impact on hydroxide density. Floc strength depends on velocity gradient in a flocculation chamber and an average floc diameter. However, it is not an average velocity gradient G in a flocculation chamber that affects the floc strength, but local velocity gradient in the area of mixing.

LEENTVAAR and REBHUN [6] investigated the strength of ferric hydroxide flocs. The results testify to a strict relationship between the floc strength and the velocity gradient G. The authors presented equation describing the maximum diameter of a floc which is generated at any value of G.

In this paper, there are given the results of research conducted both on a laboratory scale and on a pilot scale. The investigation aimed at determining the influence of flocculation time on flocs strength and their ability to adsorb organic substances dissolved in treated water. The influence of low temperature of water on the rate of floc formation and coagulation effectiveness was also examined [7]–[11].

2. SCOPE AND METHODS OF LABORATORY-SCALE INVESTIGATION

Water used in the laboratory tests was taken directly from water intake (table 1). A kind of coagulant and its optimum dose as well as a range of optimum pH were determined. Both aluminium and iron coagulants were taken into consideration.

The results of treatment were based on "jar tests". Sample volume was 1.5 dm^3. Water samples were first rapidly mixed (200 r.p.m.) for 1 minute, then slowly mixed (10 r.p.m.) for 30 minutes and finally subjected to 30-minute sedimentation. Visual observations of flocculation process were made based on a conventional scale.

Several parameters, i.e. pH, colour, turbidity, residual aluminium, permanganate oxygen demand (POD) and absorbance at 254 nm, of the samples filtered through a 45-μm membrane were analysed to estimate treatment effectiveness.

At the optimum coagulant dose and the optimum pH the investigations of the influence of temperature and flocculation time on the effectiveness of organic substances' removal from water were started. In order to assess whether a conventional coagulation occurred exclusively, the same water but with much lower dose of coagulant was subjected to the same investigation. This dose was determined for direct filtration under operating conditions in a pilot-scale system (filter and hydraulic parameters were the same as those in the conventional system). It was assumed that when a coagulant dose was too low, no visible flocs were produced, because this dose could be effective in a direct filtration only. In this case, only microflocs which also are able to absorb contaminants may appear. The tests were carried out at two different values of temperature, i.e. at 5 °C and 18 °C.

The phenomena observed during tests were analysed on the basis of absorbance changes, both in filtered and non-filtered samples. The values of the absorbance of samples filtered through a 45-μm membrane, measured at 254 nm with UV-VIS spectrophotometer, were treated as an indicator of dissolved organic contaminants in water (in this way, organic compounds with aromatic rings were determined). Flocculation time at a higher flocculant dose was 2 hours, and at a lower dose flocculation lasted one hour.

Simultaneously, the rate of coagulant hydrolysis, depending on water temperature, was also tested. To that end the pH and water alkalinity were measured. The measurements started 30 seconds after coagulant dosing. They were continued until a maximum decrease in alkalinty (as the result of coagulant hydrolysis) was reached.

3. SCOPE AND METHODS OF PILOT-SCALE INVESTIGATIONS

The pilot-scale investigations were conducted in water treatment plant supplied with water from the water intake (table 2). A temperature of raw water changed in the range of 2–16 °C, because the investigations were carried out in various seasons. In this paper, only two series of measurements were taken into consideration, i.e. the results of coagulation at water temperature of 16 °C and 6 °C. The lowest temperature of 2 °C was not taken into account because organic matter concentration measured as an absorbance was too low.

To verify the results obtained in laboratory, investigations of a conventional coagulation on the pilot scale were made. This system consisted of a rotational flocculation chamber equipped with a static system of paddles (inside diameter, $13.8 \cdot 10^{-2}$ m, working height, 2.05 m), a vertical sedimentation tank (inside diameter, $40 \cdot 10^{-2}$ m, working height, 2.1 m) and a pressure rapid filter (inside diameter, $9 \cdot 10^{-2}$ m, working height, 2.1 m). The filter bed, 1.1 m in heigh, consisted of two layers, i.e. sand and anthracite, each of 0.55 m. In order to determine the optimum hydraulic parameters of system operation, their values were changed in wide ranges (flocculation time, from 12 to 20 minutes, ascending velocity in a clarification zone of sedimentation tank, from

0.22 to 0.33 mm/s, filtration rate, from 5 to 8 m/h) taking into consideration the optimum kind and dose of coagulant and the optimum pH measured in laboratory conditions. However, to confirm that the dosage is proper, in the pilot-scale investigations jar tests were made just before each measuring series. The dose was determined on the basis of visual observations and the results of analyses of treated water. This was necessary because of the significant changes in physical and chemical water composition.

The water quality was estimated based on the changes of its main parameters. They are as follows: pH, colour, turbidity, alkalinity, residual aluminium, permanganate oxygen demand (POD) and absorbance measured at 254 nm (UV_{254}) in filtered (through a 45-μm membrane) and non-filtered samples. For some samples total organic carbon (TOC) and dissolved organic carbon (DOC) were determined.

To explain the phenomenon of distinct deterioration of the effectiveness of conventional coagulation under low temperature conditions the absorbance was measured in the flocculation chamber (samples were taken at various depths), in water flowing out from the sedimentation tank and from the rapid filter. At the same time the concentration of a residual soluble coagulant was controlled.

4. DISCUSSION AND RESULTS OF THE LABORATORY INVESTIGATIONS

The laboratory investigations revealed that in the test on the influence of flocculation time and temperature on treatment effectiveness in conventional coagulation, the dose of aluminium sulphate woul be as high as 3.2 mg Al/dm^3 at pH range of 6.0–7.0. A proper choice of pH was confirmed by residual concentration of aluminium (figure 1).
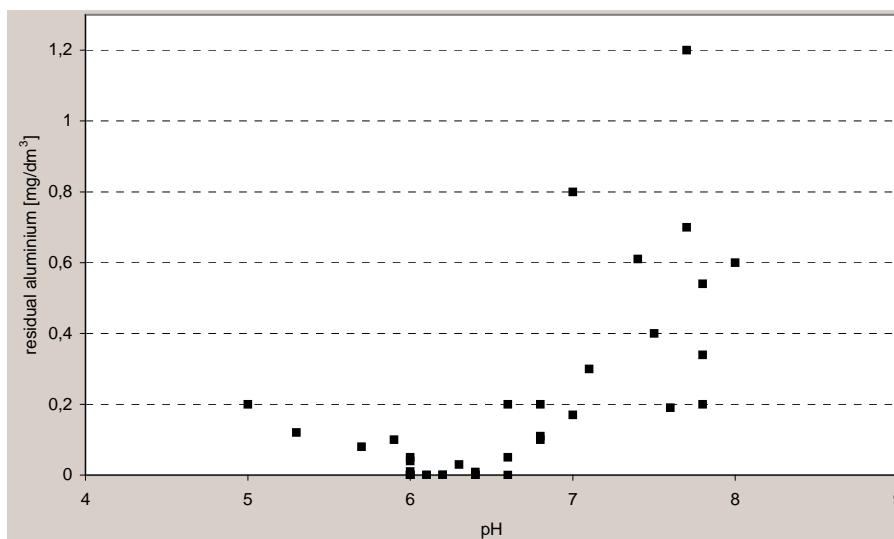

Fig. 1. Influence of pH on residual aluminium concentration

In this series, absorbance of raw water, both in filtered and non-filtered water samples, assumed the same value, i.e. 0.11 cm^{-1} (table 1). This proved that all organic substances in water were either dissolved or assumed a colloidal form. In the next part of the discussion of results, the term *absorbance* is related to filtered samples. Water was taken directly from its intake where its temperature was 5 °C. Therefore, to compare the results of the flocculation at 5 °C with the results obtained at a higher temperature, raw water was left in room conditions until its temperature reached 18 °C.

The results indicate that flocculation greatly depends on raw water temperature (figure 2). At 18 °C after 10 minutes most of dissolved organic substances was absorbed on hydroxide flocs formed which was proved by a decrease of absorbance in a filtered sample from 0.11 cm^{-1} to about 0.05 cm^{-1} (figure 2). The continuation of the flocculation did not improve its effectiveness. After 2-hour flocculation the absorbance was still the same. Hence, it can be concluded that prolonging the flocculation time over 10 minutes is useless and does not influence the removal of organic matter in the process of sorption.
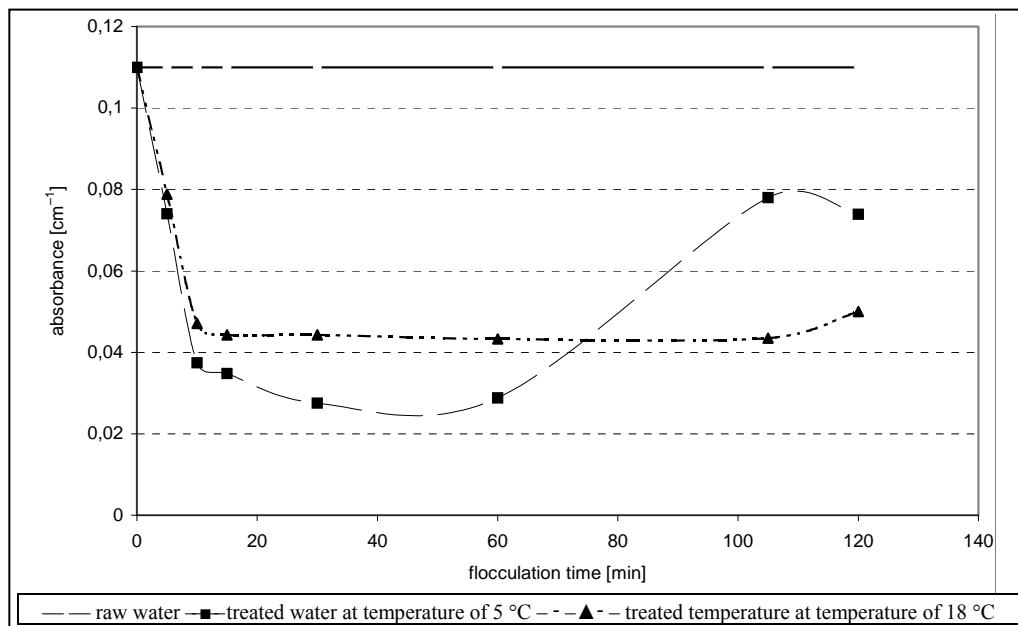

Fig. 2. Influence of flocculation time on absorbance changes (filtered samples) during coagulation at a dose of 3.2 mg Al/dm^3 (a laboratory scale)

The results obtained for the water whose temperature reached 5 °C were quite different. During slow mixing no flocs were observed. However, the absorbance meas-

urements proved that microflocs were formed, but they were too small to be visible (figure 2). The values of absorbance of the filtered samples proved that the contaminants were sorbed by microflocs a few minutes after coagulant dosing. After 10 minutes the absorbance reached the value a bit lower than that of water whose temperature was 18 °C, but the maximum decrease in absorbance (about 0.03 cm^{-1}) was measured after 30 minutes. This absorbance value was on the same level for next 30 minutes. Afterwards desorption of contaminants started (absorbance increased) and after 100 minutes approached 0.08 cm^{-1}. This proved that the temperature of 5 °C the process of flocs ageing started after 60-minute flocculation. Such a phenomenon was not observed even after 2-hour flocculation of water at 18 °C.

Taking into account the above results, it can be concluded that water temperature strongly influences the course and effectiveness of flocculation. Low temperature accelerates microflocs ageing and inhibits their agglomeration.

In order to prove that a coagulant hydrolysis proceeds independently of water temperature, the changes of alkalinity after coagulant dosing (3.2 mg Al/dm^3) have been measured. It was proved that as early as after 30 seconds the alkalinity of water both at 18 °C and 5 °C decreased by about 0.4 mval/dm^3. This value is comparable with a theoretical value resulting from the stoichiometric equation representing reaction of aluminium sulphate with compunds responsible for water alkalinity.
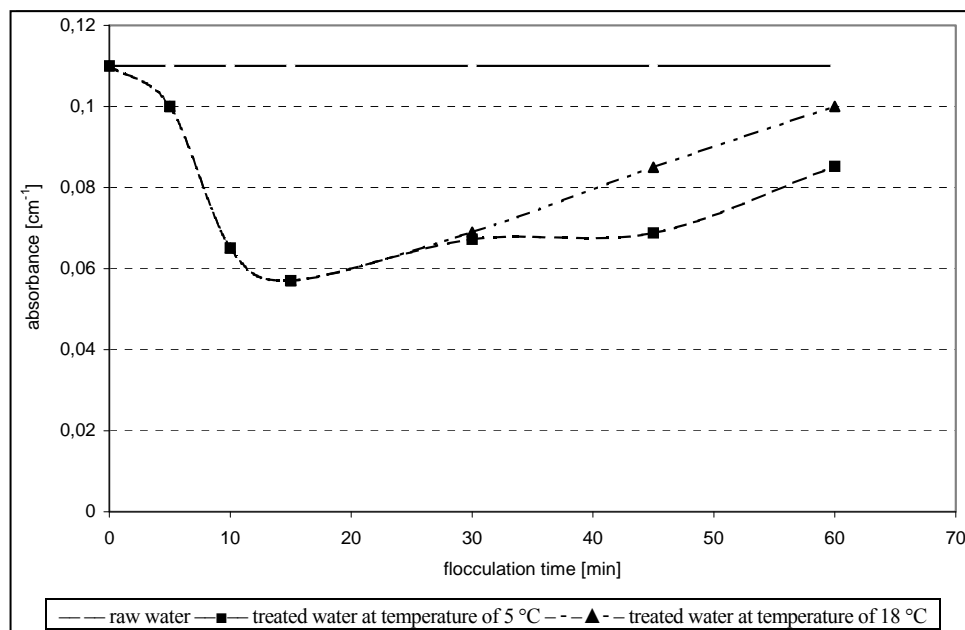

Fig. 3. Influence of flocculation time on absorbance changes (filtered samples) during coagulation
at a dose of 0.8 mg Al/dm^3 (a laboratory scale)

Totally different course of flocculation was observed at a lower coagulant dose, i.e. 0.8 mg Al/dm^3, which was predetermined for a direct filtration. As anticipated, independently of water temperature, no visible flocs were formed. However, measurements of absorbance and alkalinity proved that flocs of hydroxides were produced (figure 3). In contrast to the series with the dose of 3.2 mg Al/dm^3, a temperature had no significant impact on the flocculation course. After 15 minutes of slow mixing both at 5 °C and 18 °C a decrease in absorbance from 0.11 cm^{-1} to about 0.06 cm^{-1} was observed (in comparison with the changes of absorbance which at the dose of 3.2 mg Al/dm^3 after 15-minute flocculation decreased to about 0.04 cm^{-1}). From that time desorption of contaminants started (absorbance increased). After 60 minutes absorbance increased to 0.09–0.1 cm^{-1}, which was only slightly lower than that for raw water (0.11 cm^{-1}).

The results of tests conducted on the laboratory scale indicate that a temperature of water strongly influences the flocculation course at the optimum coagulant dose determined for a conventional coagulation (3.2 mg Al/dm^3). In the water whose temperature is low, microflocs are disaggregated, which causes desorption of contaminants.

At the dose determined for a direct filtration (0.8 mg Al/dm^3) temperature is not so important in organic matter removal. For such a low dose, independently of water temperature, visible flocs cannot be produced; however, the absorbance changes testify to the sorption of organic contaminants on aluminium hydroxide microflocs and their desorption with the time of flocculation.

5. RESULTS AND DISCUSSION OF THE PILOT-SCALE INVESTIGATIONS

Based on of the optimum technological parameters determined in the jar tests, optimum hydraulic parameters of conventional coagulation were determined in the pilot-scale tests (flocculation time, 18 minutes; rising velocity in a clarification zone of sedimentation tank, 0.22 mm/s; filtration rate, 6 m/h). At the optimum hydraulic parameters treatment process was conducted at the doses of 3.2 mg Al/dm^3 at 16 °C and 4.0 mg Al/dm^3 at 6 °C. The results of the pilot-scale investigations confirm the main conclusion from the laboratory-scale investigations that independently of raw water temperature the coagulant is hydrolysed almost immediately and aluminium hydroxide microflocs, which are capable of absorbing organic contaminants, are formed. This was proved by the measurements of absorbance in filtered samples taken from the flocculation chamber (at various depths) and from the flocculation chamber outlet in two different series (at temperature of 6 °C and 16 °C). Because the values of absorbance measured in water from the flocculation chamber and from the flocculation chamber outlet are similar, only absorbance changes in the outlet are given (figures 4 and 5). Both at the temperature of 16 °C and 6 °C in the flocculation chamber, the absorbance of filtered samples decreased from 0.08–0.09 cm^{-1} to 0.03–0.04 cm^{-1}. A considerable influence of temperature on

absorbance was observed with time. At the temperature of 6 °C in the sedimentation tank, organic matter concentration increased. An average value of absorbance of filtered samples increased from 0.03–0.04 cm^{-1} in the flocculation chamber outlet to about 0.06 cm^{-1} in the sedimentation tank outlet (the first 6 hours were considered to be the time of the system adjustment to the operation under the optimum technological and hydraulic conditions). These values also increased in unfiltered samples (figures 5 and 7). This proves that low temperature is responsible for the desorption of dissolved organic contaminants and microflocs disaggregation confirmed by high concentration of residual soluble aluminium. Such a phenomenon was not observed in the series with water temperature of 16 °C. Hence, it can be concluded that temperature drop below critical value causes ageing of flocs. This conclusion is consistent with the conclusion drawn on the basis of the laboratory investigations (figure 2).
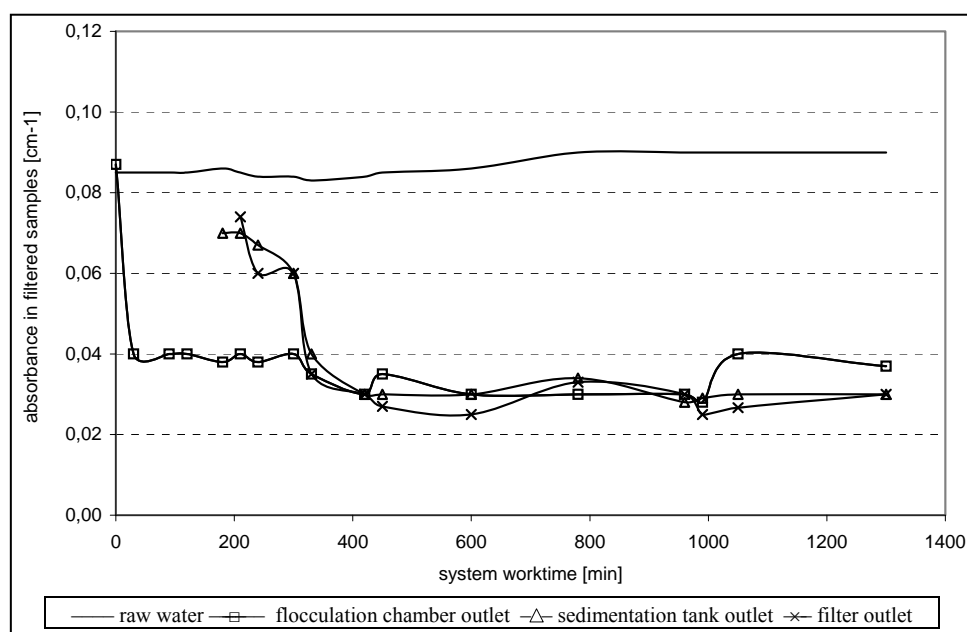

Fig. 4. Changes of absorbance values (filtered samples) in conventional coagulation
at temperature of 16 °C

At the temperature of 16 °C the filter, first of all, separated from a water the aluminium hydroxide flocs with organic contaminants absorbed on them, which was corroborated by the changes in absorbance of filtered and unfliltered samples taken from the sedimentation tank outlet and the filter outlet (figures 4 and 6). A good quality of water after its treatment in the conventional coagulation system, consistent with standards for drinking water, confirmed a proper course of coagulation. Turbidity was totally removed (its value for raw water ranged from 4 to 10 NTU); only its temporary

increase to 0.7 NTU was observed. At the same time all the contaminants responsible for the water turbidity (in raw water it ranged from 20 to 25 mg Pt/dm^3) were removed. After 16-hour operation of the system the experiment was complete. This time POD reached 1.2 mg O$_2$/dm^3 (3.0–3.7 mg O$_2$/dm^3 in raw water).
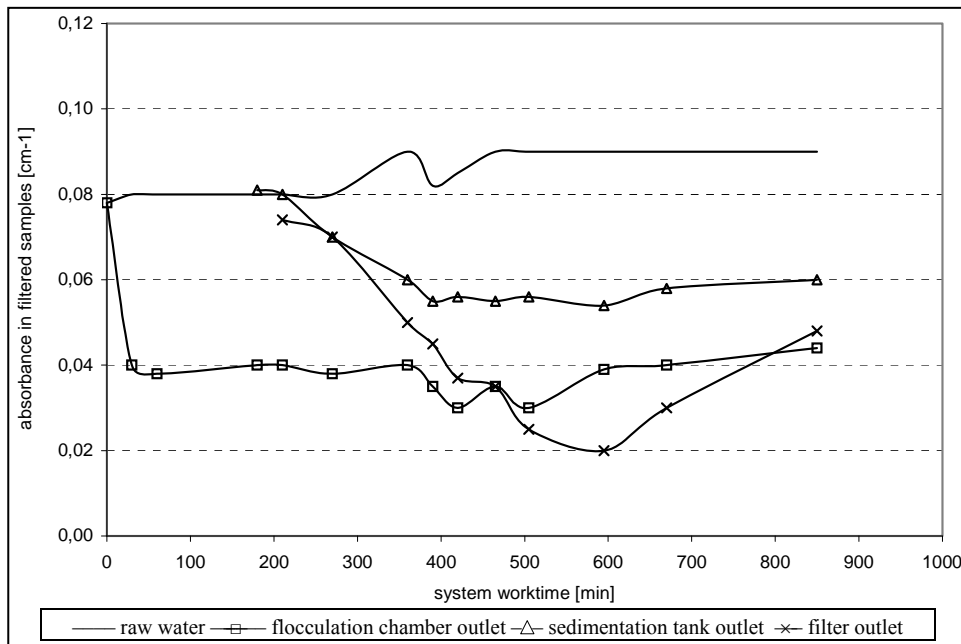

Fig. 5. Changes of absorbance values (filtered samples) in conventional coagulation
at temperature of 6 °C

At the temperature 6 °C the process of water treatment was inhibited (water quality parameters did not meet the standards). For a very short time only the dissolved organic conatminants passed through a filter (absorbance decreased to 0.03 cm^{-1}) which was caused by absorbing capacity of the filter (figures 5 and 7). The values of absorbance of filtered and unfliltered samples drawn from the sedimentation tank outlet were very similar, so it can be assumed that all organic matter in water flowing to the filter was dissolved. An improver course of coagulation resulted in a poor quality of water after its treatment. In the first period of treatment, the turbidity of water after its filtration increased from 1 NTU to 3 NTU. Similar unsiderable changes were observed for the other parameters. Though the water turbidity decreased temporarily (even from 20 mg Pt/dm^3 to zero), but afterwards it immediately increased. At the same time a maximum decrease in POD (to 0.7 mg O$_2$/dm^3) was observed; in raw water, POD ranged from 2.7 to 2.9 mg O$_2$/dm^3. However, this effect lasted too short, hence it could not be taken into account in the evaluation of the treatment effectiveness.
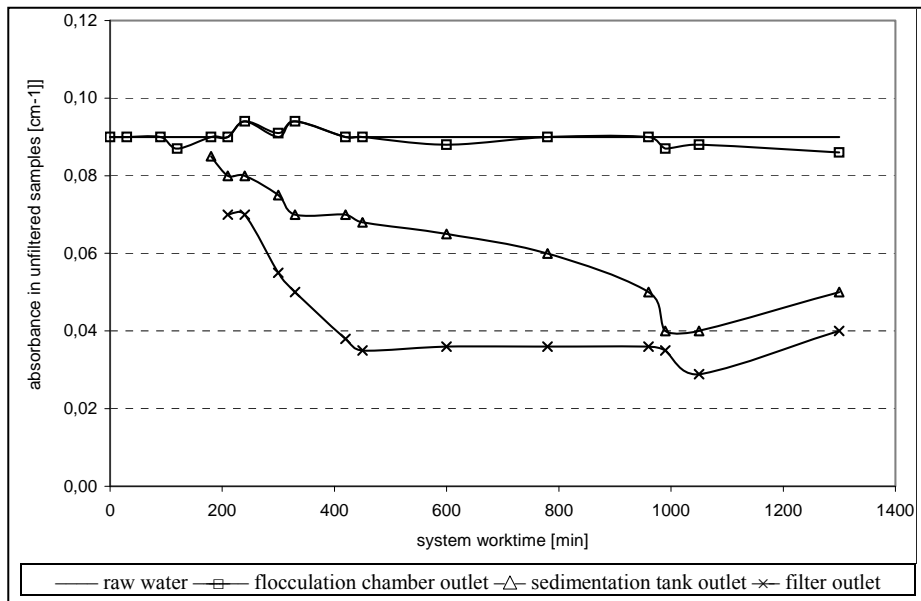
Fig. 6. Changes of absorbance values (unfiltered samples) in conventional coagulation
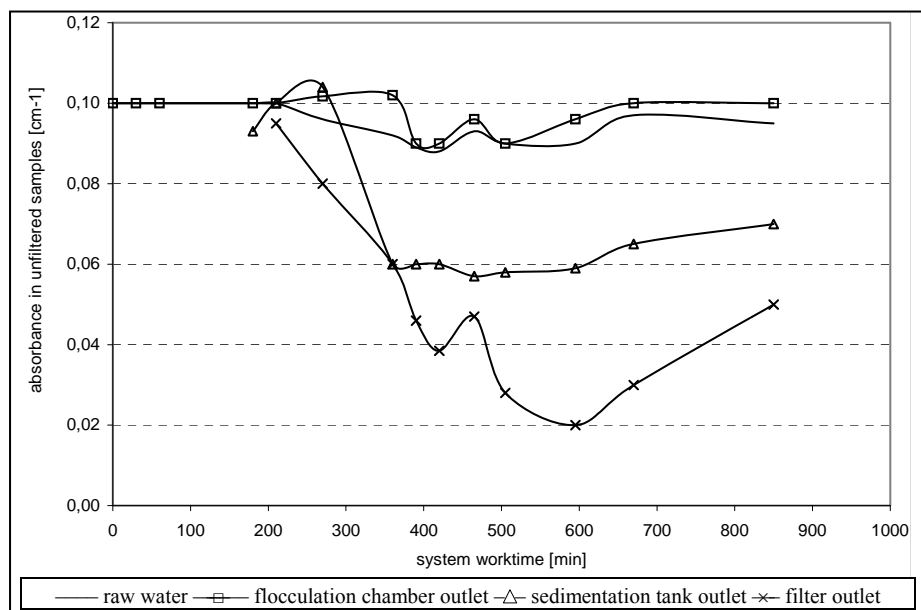at temperature of 16 °C

Fig. 7. Changes of absorbance values (unfiltered samples) in conventional coagulation
at temperature of 6 °C

6. CONCLUSIONS

During conventional coagulation temperature is one of the crucial parameters which influence course and effectiveness of treatment. Although independently of the temperature of treated water the coagulant is hydrolysed and hydroxide flocs are formed, below the critical temperature these flocs are instable and their disaggregation starts.

LITERATURE

[1] HUDSON H., *Water Clarification Processes*, Van Nostrand Reinhold Company, 1981.

[2] LICSKO I., *Microprocesses in coagulation*, Water Research, 1976, 10, 143–1147.

[3] FRANÇOIS R., VAN HAUTE A., WINDERICK G., *The Influence of Kinetic Process Parameters on Flocculation Characreristics*, The Practical Theory of Flocculation Processes, K.U. Leuven, 1981.

[4] FRANÇOIS R., BEKAERT N., *Ageing of Aluminium Hydroxide Flocs*, Water Research, 1987, 5, 523–531.

[5] FRANÇOIS R., BEKAERT N., *Strength of Aluminium Hydroxide Flocs*, Water Research, 1987, 9, 1023–1030.

[6] LEENTVAAR J., REBHUN M., *Strength of Ferric Hydroxide Flocs*, Water Research, 1983, 8, 895–902.

[7] DRYFUSE M., MILTNER R., SUMMERS R., *The Removal of Molecular Size and Humic/Non-Humic Fractions of DPD Precursors by Optimized Coagulation*, Proceedings of the American Water Works Annual Conference, Anaheim, 1995.

[8] *EPA Guidance Manual. Manual for Enhanced Coagulation and Precipitative Softening*, 1999.

[9] KORSHIN G., LI Ch., BENJAMIN M., *The Decrease of UV Absorbance as an Indicator of TOX Formation*, Water Research, 1997, 4.

[10] OLLIS D., PELIZZETTI E., SERPONE N., *Destruction of Water Contaminants*, Env. Sci. Eng., 1991, 9, 1523–1529.

[11] ŚWIDERSKA-BRÓŻ M., *Wybrane problemy w oczyszczaniu wody do picia i na potrzeby gospodarcze*, Ochrona Środowiska, 1999, 3(74), 7–12.

PROCES STARZENIA SIĘ KŁACZKÓW
I JEGO WPŁYW NA SKUTECZNOŚĆ FLOKULACJI

Skuteczność koagulacji objętościowej zależy przede wszystkim od trwałości powstających kłaczków oraz ich zdolności do sorbowania zanieczyszczeń z wody. Na podstawie uzyskanych wyników badań stwierdzono, że niezależnie od temperatury wody surowej następuje hydroliza koagulanta i wytrącają się kłaczki wodorotlenku glinu sorbujące zanieczyszczenia. Jednak z upływem czasu w wodzie o niskiej temperaturze następuje ich desorpcja i rozpad mikrokłaczków, a więc proces koagulacji jest nieskuteczny.