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# Cationic Flocculants Carrying Hydrophobic Functionalities: Applications for Solid/Liquid Separation<sup>†</sup>

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The flocculation behaviors of three series of polycations with narrow molecular weight distributions carrying hydrophobic substituents on their backbones [poly(*N*-vinylbenzyl-*N,N,N*-trimethylammonium chloride), poly(*N*-vinylbenzyl-*N,N*-dimethyl-*N*-butylammonium chloride), and poly(*N*-vinylbenzylpyridinium chloride)] were investigated in dispersions of monodisperse polystyrene latexes and kaolin. Apparently, the charge density of the polycations decreases with increasing substituent hydrophobicity and increasing molecular weight of the polyelectrolytes. The necessary amount of flocculant for phase separation in dispersions with high substrate surface charge densities increases with increasing hydrophobicity of the polyelectrolyte. Nevertheless, the introduction of hydrophobic functionalities is beneficial, resulting in a substantial broadening of the range between the minimum and maximum amounts of flocculant necessary for efficient flocculation (flocculation window). An increase in ionic strength supports this effect. When the substrate has a low charge density, the hydrophobic interactions play a much more significant role in the flocculation process. Here, the minimum efficient doses remained the same for all three polyelectrolytes investigated, but the width of the flocculation window increased as the polycation hydrophobicity and the molecular weight increased. The necessary amount of flocculant increased with an increase in particle size at constant solid content of the dispersion, as well as with a decreasing number of particles at a constant particle size.

## Introduction

Solid–liquid separation by coagulation and flocculation is an important part of many technical processes. Typical examples are wastewater treatment and sludge dewatering; pulp and paper production; and the pharmaceutical, cosmetics, and metal-working industries. The overwhelming majority of these processes use polyelectrolytes to regulate the stability and flocculation properties of the disperse systems. This results in a great variety of synthetic flocculants that are now commercially available to meet the specific demands of industrial fields in which efficient solid–liquid separation is required.<sup>1,2</sup> The results of both fundamental and application-oriented investigations have been the subject of numerous articles and patents (e.g., refs 3–13) and have been summarized in several reviews.<sup>1,14–16</sup>

The flocculation process is determined by several different parameters: molecular weight and charge density of the polyelectrolytes, ionic strength of the solution, and size and surface charge of the dispersed particles.<sup>1,5,7,12</sup> These parameters mainly determine the conformation of the adsorbed polyelectrolytes and the charges of the polyelectrolyte-covered particles, which have a key influence on the stability and the flocculation behavior of the suspension.<sup>5,7,17–22</sup> The flocculation process is often described by a simple model, distinguishing between

bridging and charge neutralization.<sup>1,16</sup> Polyelectrolytes with low charges are usually assumed to destabilize colloidal dispersions through bridging of neighboring particles by adsorbed polymers in loose conformations with numerous loops and tails dangling into the solution. Obviously, the efficiency of flocculation in such systems depends strongly on the molecular weight of the polymer. As the charge density of the polyelectrolyte increases, the charge interactions become more important. The polyelectrolyte tends to adsorb in a very flat conformation. Flocculation occurs as a result of surface charge neutralization or the attraction of oppositely charged patches on partially covered particles. In this case, adsorption, and thus flocculation efficiency, does not depend markedly on the molecular weight.<sup>23</sup>

Most industrial solid–liquid separations are carried out by well-established processes using highly hydrophilic linear polymers with good solubilities in water. Nevertheless, there are still two essential deficiencies in this field.<sup>24</sup> First, the flocculation range (flocculation window), that is, the range between minimum and maximum amounts of flocculant resulting in sufficient separations, is often very small, thus bearing the risk of restabilization of the particles through an overdosage of the flocculant. Second, some special separation problems which have not yet been sufficiently solved, e.g., those concerning suspensions containing small particles with low surface charges or suspensions containing high amounts of disturbing additives such as tensides, oils, stabilizers, dyes, etc. A general tendency of the past several years to overcome these disadvantages and to increase the performance of many well-established separation processes is to optimize the solution properties of the polyelectrolytes by varying their molecular

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**TABLE 1: Substrates Used for the Flocculation Investigations**

substrate	particle size (nm) <i>z</i> average (PCS)	polydispersity	surface charge density ( $\mu\text{C}/\text{cm}^2$ )	polymerization method <sup>a</sup>
PSL 139	225	0.04	−2.3	classical emulsion polymerization
PSL 140	221	0.03	−7.3	
PSL 181	506	0.09	−8.0	emulsion copolymerization
PSL 179	909	0.09	−10.0	emulsifier-free polymerization
kaolin	8500	—	−6.4	emulsifier-free polymerization

<sup>a</sup> Heterophase polymerization in water.**TABLE 2: Polyelectrolytes Used as Flocculants**

Polymer Polyvinyl- benzyl-	structure	$P_n = 98$	$P_n = 164$	$P_n = 638$	$P_n = 1400$
trimethyl- ammonium chloride  PVB- TMAC		<b>PVB- TMAC 98</b>  CD 4.9 [meq/g]	<b>PVB- TMAC 164</b>  CD 4.7 [meq/g]	<b>PVB- TMAC 638</b>  CD 4.6 [meq/g]	<b>PVB- TMAC 1400</b>  CD 4.5 [meq/g]
dimethyl- butyl- ammonium chloride  PVB- DMBAC		<b>PVB- DMBAC 98</b>  CD 4.3 [meq/g]	<b>PVB- DMBAC 164</b>  CD 4.0 [meq/g]		<b>PVB- DMBAC 1400</b>  CD 3.4 [meq/g]
pyridinium chloride  PVB-PYC		<b>PVB- PYC 98</b>  CD 4.6 [meq/g]	<b>PVB- PYC 164</b>  CD 4.3 [meq/g]		<b>PVB- PYC 1400</b>  CD 2.1 [meq/g]

architecture. Cationic polyelectrolytes containing small amounts of long chain branches show better application properties,<sup>25</sup> obviously because of the higher charge density in the coil. Furthermore, the introduction of hydrophobic parts enhances the flocculation properties of ionic polymers<sup>4</sup> and results in a broader flocculation window.<sup>5,12,24</sup>

In this article, we report on the flocculation performances of three series of new cationic polyelectrolytes with quaternary ammonium groups and different hydrophobic substituents. The polymerization degree was varied in each series to facilitate the evaluation of the flocculation mechanism and allow the optimization of the flocculant design to reach the highest efficiency in solid–liquid separations.

## Experimental Section

**Materials. Substrates.** Polystyrene latexes with different amounts of surface sulfate groups were obtained by classical emulsion polymerization of styrene using sodium dodecylsulfate as the emulsifier and potassium peroxodisulfate as the initiator by emulsion copolymerization of styrene with sodium styrene sulfonate and by emulsifier-free polymerization of styrene as described in ref 26. Kaolin (TEC FF 840 type) was supplied by Kaolinwerk Amberg (Amberg, Germany) and used as received. The characteristics of the substrates are listed in Table 1.

**Polyelectrolytes.** The synthesis of the cationic polyelectrolytes was performed in two steps. First, the reactive precursor polymer

poly(vinylbenzyl chloride) (p-VBC) was synthesized using controlled free-radical polymerization followed by polymer-analogous reactions as the second step. This procedure has several advantages. First, polymers with narrow molecular weight distributions are obtained, thus improving and facilitating any physicochemical measurements. Second, size-exclusion chromatography (SEC) measurement of the precursor polymer is well-established compared to the direct determination of the molecular weight of hydrophobic polyelectrolytes. Thus, precise data are available for these polyelectrolytes, too.

The controlled free-radical polymerization of vinylbenzyl chloride (mixture of meta and para isomers)<sup>27</sup> resulted in p-VBC with degrees of polymerization ( $P_n$ ) of 98, 164, and 638. Additionally, a polymer with a larger  $P_n$  ( $P_n = 1400$ ) was prepared by conventional free-radical polymerization.<sup>27</sup> Subsequent reaction with trimethylamine, dimethylbutylamine, or pyridine led to poly(*N*-vinylbenzyl-*N,N,N*-trimethylammonium chloride) (PVB-TMAC), poly(*N*-vinylbenzyl-*N,N*-dimethyl-*N*-butylammonium chloride) (PVB-DMBAC), and poly(*N*-vinylbenzylpyridinium chloride) (PVB-PYC), respectively,<sup>27,28</sup> as listed in Table 2. The degree of functionalization was above 95% as revealed by <sup>1</sup>H NMR spectroscopy.

**Methods. Photon Correlation Spectroscopy (PCS).** PCS measurements were performed at a scattering angle of 90° with a Zetasizer 3000 instrument (Malvern Instruments Ltd., Malvern, U.K.) equipped with a 10 mW He–Ne laser as a light source.

The operating wavelength was 633 nm. The analysis of autocorrelation function  $g^2(\tau)$  was done automatically to yield diffusion coefficients that allowed for the calculation of the apparent mean hydrodynamic diameters of particles according to the Stokes–Einstein equation.

**Polyelectrolyte Titration.** The charge densities of polyelectrolytes and latex particles were determined by colloid titration in a particle charge detector (PCD-03, Müttek, Herrsching, Germany) combined with a 702 SM Titrino (Metrohm, Herisau, Switzerland). Solutions containing low-molecular-weight sodium polyethylene sulfonate (PES-Na) or poly(*N,N*-diallyl-*N,N*-dimethylammonium chloride) (PDADMAC) were used as titrants for cationic or anionic systems, respectively. The charge density (CD) (mequivq·g<sup>-1</sup>) was calculated according to the formula:

$$CD = C_{\text{titrant}} V_{\text{titrant}} / Vm$$

where  $C_{\text{titrant}}$  is the concentration of titrant (mequiv·L<sup>-1</sup>),  $V$  is the volume of titrated solution,  $V_{\text{titrant}}$  is the equivalent titrant volume (L), and  $m$  is the content of polyelectrolytes or substrate in the titrated solution (g·L<sup>-1</sup>).

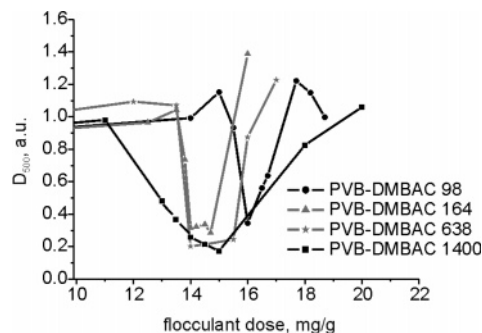
**Flocculation.** Flocculation was investigated as a batch test in series of beakers each containing 50 mL of dispersion. The solid content of the dispersions was 0.1, 0.2, or 1 g·L<sup>-1</sup>, and the ionic strength was varied from 0 to 0.1 M NaCl depending on the experimental series. To complete the phase separation, after the addition of aliquots to the polyelectrolyte solution, the mixtures were stirred for 15 min and then allowed to sediment. The sedimentation time of the kaolin dispersions was 20 min, and that of the latex dispersions was 1 h. Accordingly, 5 mL of the supernatant was removed from the beaker surface, and its optical density ( $D_{500}$ ) was measured at 500 nm using a Lambda 800 UV–vis spectrometer (Perkin-Elmer).

## Results and Discussion

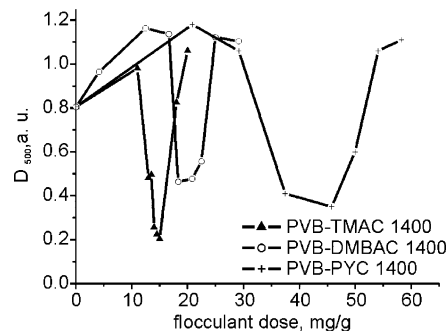
**Charge Density.** Analysis of the charge densities of the polyelectrolytes (Table 2) clearly shows that the hydrophobic substituents of the polymers affect the accessibility of the cationic charges. In an ideal case, the charge density (CD) of a linear polyelectrolyte should not significantly depend on its molecular weight, although some deviations from 1:1 stoichiometry are possible depending on the titrant/polyanion pair. This holds for PVB-TMAC, as expected. The data in Table 2 show no systematic change of the apparent charge density with increasing molecular weight for this polyelectrolyte containing only short-chain substituents at the quaternary nitrogen. However, the charge densities in the PVB-DMBAC and PVB-PYC series drop notably with increasing degree of polymerization. This important fact is in good correspondence with the cooperative nature of hydrophobic interactions, which are favored by increasing polymer molecular weight. This tendency is more pronounced for the more hydrophobic series of PVB-PYC, which contains a pyridinium ring as a substituent, thus supporting the suggestion that hydrophobic interactions in the studied polyelectrolyte series significantly affect the accessibility of the cationic charges.

**Effect of Polyelectrolyte Characteristics.** Studying the effects of various structural characteristics of a polyelectrolyte on its flocculation performance requires well-defined substrates with a single-sized particle distribution and well-known surface chemistry. This can be achieved by using dispersions of latex particles as a model, as listed in Table 1.

Figure 1 shows the flocculation behavior of PSL 140 dispersions with the hydrophobically modified polyelectrolyte



**Figure 1.** Flocculation of latex PSL 140 dispersions with the polyelectrolyte PVB-DMBAC of different molecular weights; solid content = 0.2 g/L.

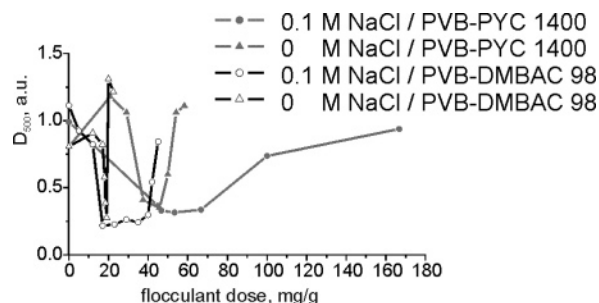


**Figure 2.** Flocculation of latex PSL 140 dispersions with flocculants of different hydrophobicities; solid content = 0.2 g/L.

PVB-DMBAC of different molecular weights as a flocculant. From typical commercial flocculants, which are highly hydrophilic and have good water solubilities even at high molecular weights, it is well-known that the efficiency usually increases with increasing molecular weight (MW). A similar influence of MW also holds for PVB-DMBAC. Remarkably, this polyelectrolyte has a comparatively lower MW than the commercial products. However, a dramatic shift in the flocculant dose is observed only when  $P_n$  increased from 98 to 164. In a previous work,<sup>12</sup> we showed that, although low-molecular-weight polycations are adsorbed on the latex particles with significant surface overcharging, there are no efficient “charge patch” interactions at intermediate coverage degrees because the polymer patches are too small. Thus, in this case, the flocculation mechanism is very close to charge neutralization. An increase of the molecular weight of the polyelectrolytes first results in the formation of larger polyelectrolyte patches, which provide more efficient attractive interactions at partial surface coverage.<sup>29</sup> Second, it can lead to loops and tails if the contour length of the polyelectrolytes, even highly charged ones, exceeds the diameter of the particles.<sup>30</sup> Both of these effects can contribute to the broadening of the flocculation window, as shown in Figure 1. With increasing molecular weight, the hydrophobic interactions increase, and the effective charge decreases, resulting in a more compact conformation of the hydrophobically associating derivatives in solution and at interfaces. Thus, we can assume that the hydrodynamic radius is larger, which leads to a broad flocculation window.

Figure 2 shows the flocculation behavior of PSL 140 dispersions using flocculants that carry different hydrophobic substituents. To evaluate the effects of the different hydrophobic modifications, the flocculation performances of three polycations with the same polymerization degree ( $P_n = 1400$ ) but varied monomer structures were compared. The results clearly indicate that an increase in polyelectrolyte hydrophobicity leads to a





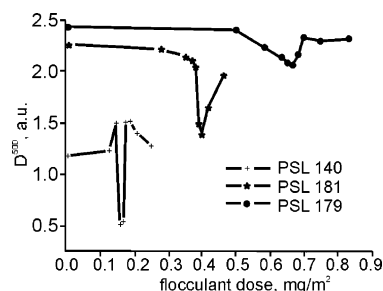
**Figure 3.** Floculation of latex PSL 140 dispersions at different ionic strengths of the solution; solid content = 0.2 g/L.

concomitant increase of the required flocculant dose and to a broadening of the flocculation window. The behavior of PVB-TMAC polycation carrying no substituents of pronounced hydrophobicity is very close to that of the highly charged polycation PDADMAC.<sup>12</sup> These flocculants are efficient in very narrow concentration ranges and then experience electrostatic restabilization at even very modest overdosing. On the contrary, the flocculation window of PVB-PYC is markedly broader. For polymers with high molecular weights and increasingly hydrophobic polycations from PVB-TMAC to PVB-PYC, the effective charge decreases dramatically to values of about 50%, as a result of increasing hydrophobic interactions. However, the optimal polymer doses for flocculation are about 50% higher. Taking into account the significant fluctuations of the parameters of industrial waste streams (solid content, ionic strength, pH value, presence of surfactants and their concentrations), which can occur within 1 day or even within 1 h, one can assume that very precise estimations and dosings of flocculants are hardly feasible. Thus, despite the higher required doses, flocculants providing a broader flocculation window can be more beneficial for industrial applications.

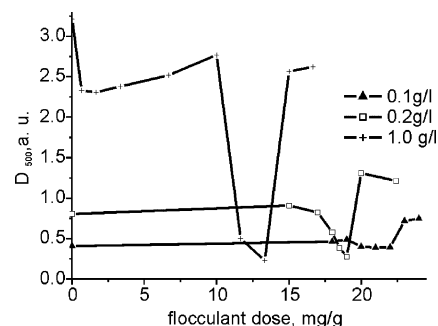
Because of today's tendency to close the water cycles of industrial applications, the ionic strengths of aqueous technical solutions tend to become increasingly higher. Thus, the effect of low-molecular-weight electrolytes on the flocculation performance is important with respect to potential industrial applications of the flocculants.

Figure 3 shows the flocculation behavior of PSL 140 dispersions in water and 0.1 M NaCl using PVB-DMBAC 98 and PVB-PYC 1400 as flocculants. The increase of the ionic strength does not affect the minimum efficient flocculant dose for either of the hydrophobically modified polymers, but it does increase the concentration ranges of the flocculants' applicability. These data indicate that screening of the electrical charge by a salt concentration of 0.1 M does not lead to a decrease in the adsorbed amount of polymer and, thus, to a reduction of the flocculation efficiency. The broadening of the unstable region in the dispersions is in good agreement with DLVO theory, as the addition of salt compresses the electrical double layer of particles and decreases their electrostatic repulsion. Thus, the number of marginally stable particles increases, and aggregation occurs in a broader concentration range of added flocculant.

**Effects of Substrate Characteristics.** Figure 4 demonstrates that the efficiency of phase separation decreases as the particle size increases. Particles of increasing size with comparable surface charge densities at a constant solid content of the dispersion require increasing amounts of flocculant and result in supernatants of higher turbidity. Although this result could have been expected according to DLVO theory,<sup>31</sup> the majority of previous experimental works<sup>32,33</sup> had not confirmed this



**Figure 4.** Dependence of the flocculation of latex dispersions on particle size: PSL 140 (221 nm), PSL 181 (506 nm), PSL 179 (909 nm). Solid content = 0.2 g/L, flocculant = PVB-DMBAC 98.

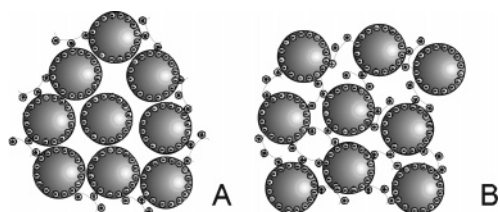


**Figure 5.** Dependence of the flocculation of latex PSL 140 dispersions with PVB-DMBAC 98 on solid content.

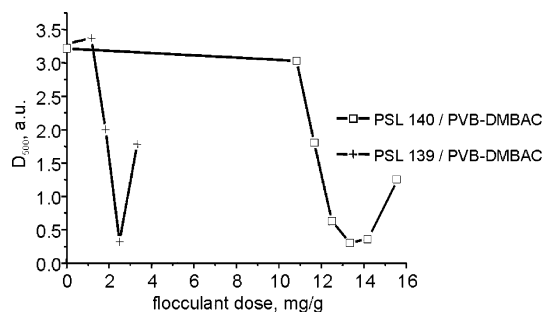
prediction. The coagulation in the secondary minimum was suggested to be the main reason for the low sensitivity of the coagulation rate to the particle size. However, a later work<sup>34</sup> found that the particle size does not determine the efficiency of interparticle collisions and the observed discrepancy in experiments originates from neglecting the hydrodynamic interactions in DLVO theory. Because the data presented in Figure 4 were obtained at fixed solid content for all latexes, we believe that the observed difference in behavior can be related directly to the decrease in the number of particles with increasing particle size and not to an increase in dispersion stability. This assumption is supported by the results shown in Figure 5 describing the flocculation dependence of PSL 140 with PVB-DMBAC 98 on the solid content. As a result of the reduced collision efficiency at larger interparticle distances, a decrease of the solid content leads to the requirement of higher flocculant doses for phase separation and a less deep minimum on the turbidity curve.

It has been shown<sup>35</sup> that, at high solid contents, a uniform coverage of the particle surface is usually not reached because of the comparable times of flocculation and polymer adsorption. If the affinity of the polymer to the substrate is high, a one-step addition of the polymer, even under vigorous agitation, results in a local polymer overdose and the formation of particle fractions with a high coverage degree at a polymer concentration that theoretically corresponds to a much lower surface coverage. This behavior is known as the surface excluded effect and is illustrated by the scheme presented in Figure 6. At a high solid content, the particles are close together. The polyelectrolytes cannot adsorb on the whole particle surface, and the adsorbed amount is much lower.

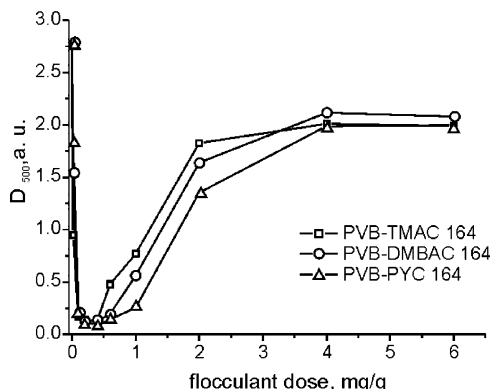
Figure 7 shows that, in the case of hydrophobically modified flocculants, the flocculant dose required for phase separation is also proportional to the substrate charge density. This finding confirms the governing role of electrostatic interactions in the studied systems as well. Additionally, one must keep in mind that higher flocculant doses are required if the hydrophobicity



**Figure 6.** Schematic representation: Dependence of the adsorption of polymer on the solid content of the dispersion. (A) High solid content, low particle–particle distance. (B) Moderate solid content.



**Figure 7.** Flocculation of latex dispersions carrying different charge densities: PSL 140, PSL 139. Flocculant = PVB-DMBAC 98.



**Figure 8.** Flocculation of kaolin with flocculants of different hydrophobicities.

of the polycations increases and some of the positive charges are screened from interactions (Figure 2). The beneficial effect of the hydrophobic functionalities is the broadening of the width of the flocculation window.

With inorganic substrates, such as kaolin, the hydrophobicity of the polyelectrolytes has a more significant role in the flocculation efficiency. At the same minimum efficient dose, flocculants with higher hydrophobicities provide broader flocculation windows (Figure 8). This effect becomes more significant as the molecular weight of the polyelectrolyte increases because of the cooperative nature of the hydrophobic interactions.

## Conclusions

Three series of hydrophobically modified cationic polyelectrolytes with narrow molecular weight distributions, varying in type of hydrophobic functionality and molecular weight, were synthesized via controlled free-radical polymerization of a reactive monomer, followed by different modification reactions of the precursor polymer. The poly(*N*-vinylbenzyl-*N,N,N*-substituted ammonium chlorides) that contain three substituents of different hydrophobicities show a decrease of the apparent charge density of up to 50% with increasing hydrophobicity and molecular weight. Flocculation investigations with mono-

disperse latex dispersions of different particle sizes and surface charge densities as well as stable kaolin dispersions reveal higher amounts of adsorbed polymers and a pronounced increase of the range between the minimum and maximum amounts of flocculant necessary for an effective flocculation (flocculation window). These findings can be related to the more compact conformations of hydrophobically associating derivatives in solution and at interfaces. The beneficial effect of hydrophobic substitution was found to be more significant in the flocculation of kaolin dispersions, where the surface charge density was significantly lower. In particular, the substantial broadening of the flocculation window offers possibilities to overcome disadvantages of some of today's industrial flocculation processes such as restabilization of particles as a result of an overdose of the flocculant.

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