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ORIGINAL CONTRIBUTION

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Optimization of the use of polyelectrolytes for dewatering industrial sludges of various origins

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Abstract Four different industrial slurries were flocculated with polymeric flocculating agents (port sediment, sewage sludge, sugar beet washings and an aluminum hydroxide suspension). The quantities of flocculating agent employed were optimized with the aid of a patented, portable flocculation and dewatering apparatus. Using sewage sludge as an example, it was possible to arrive at predictions for particular doses of flocculating by means of a combined method of dewatering experiments and electrokinetical measurements. The results of monoflocculation and dual flocculation made it possible to deduce that there are similarities in the flocculation and dewatering behavior of slurries with comparable parameters.

Comparison of the sediment particles and the polymer coils revealed a size ratio of 60:1, with the former being the larger. This was then used to devise modifications to the patch charge model and the bridging model as a function of the molar mass of the flocculating agent. The modifications were found to agree well with the experimental findings and the structural conceptions of macromolecular substances.

Key words Polyelectrolytes – flocculation – solid–liquid separation – zeta-potential – bridging model – patch charge model

Introduction

Polyelectrolytes are currently used for the separation of suspended particles that are difficult to sediment. A large range of these so-called flocculating agents with different chemical properties for numerous separation problems are commercially available.

Examples of aqueous suspensions include sewage sludge from municipal effluent [1–5], dredged mud from the maintenance of waterways [6–9], sugar beet washings from sugar extraction and effluent from the production of offset printing plates. The quantities of these slurries generated annually are given in Table 1. They illustrate the great potential for the use of flocculating agents, since the large volumes involved – not to mention the content of pollutants – mean that dewatering cannot simply be abandoned.

Clarification of effluent by simple filtration or centrifugation is not possible due to the partially colloidal nature of the suspended particles (small size, like charges). Satisfactory mechanical solid/liquid separation can only be achieved by prior coagulation of the colloid, i.e., by flocculation, which is generally carried out by the addition of oppositely charged polyelectrolytes [10, 11]. These destabilize the suspensions by the combination of two mechanisms:

- reduction of the electrostatic repulsion between the particles by charge compensation
- aggregation of the particles.

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Table 1 Annual volumes and total solids (TS) contents of some aqueous slurries in 1995

Slurry	Volume 10^6 m^3/a	TS t/a	TS %
Dredged mud from the deepening of the navigation channel of the River Elbe in Hamburg harbour [6, 7]	2.5	600 000	12
Sewage sludge from municipal effluent:			
FRG [8]	50	2 200 000	3 ... 5
Hamburg [9]	1.5	40 000	3 ... 3.5
Aluminum hydroxide slurry from the litho-aluminum production of an offset printing plate factory in south Germany	0.36	600	0.5 ... 1
Sugar beet washings from a sugar factory in south Germany	0.4	50 000	10 ... 15

Both effects accelerate the sedimentation of the solids. This plays a role in sedimentation basins (see Fig. 1) and during mechanical dewatering in centrifuges. When belt screen presses are used, adequate floc size is one of the basic requirements for successful dewatering in order to prevent the flocs slipping through the filter fabric.

The various commercially available flocculating agents differ in their molar mass, charge density and chemical structure. The wide range of available preparations shows that there is no universal agent for all separation problems. The cause of this is to be found in the fact that slurries exhibit very different patterns of properties, the parameters and methods of determination for which are listed in Table 2.

Table 2 Compilation of the important parameters affecting slurries and suitable methods for their measurement

Parameter	suitable measurement procedure
Content of total solids	drying and weighing
Loss on ignition (organic content)	ignition and weighing
Sign of charge	measurement of zeta potential
Particle size distribution	laser diffractometry
Salt content	analysis of filtrate
Mineralogical composition	X-ray diffraction, disintegration processes
Chemical composition	wet analysis, spectroscopic methods

It has hitherto not been possible to theoretically deduce the required properties of the flocculating agent by means of the slurry parameters. The choice of preparation for a special separation problem as well as the determination of the optimum concentration to be used is therefore still carried out empirically.

During the investigations involved in this study a patented flocculation and dewatering apparatus was used

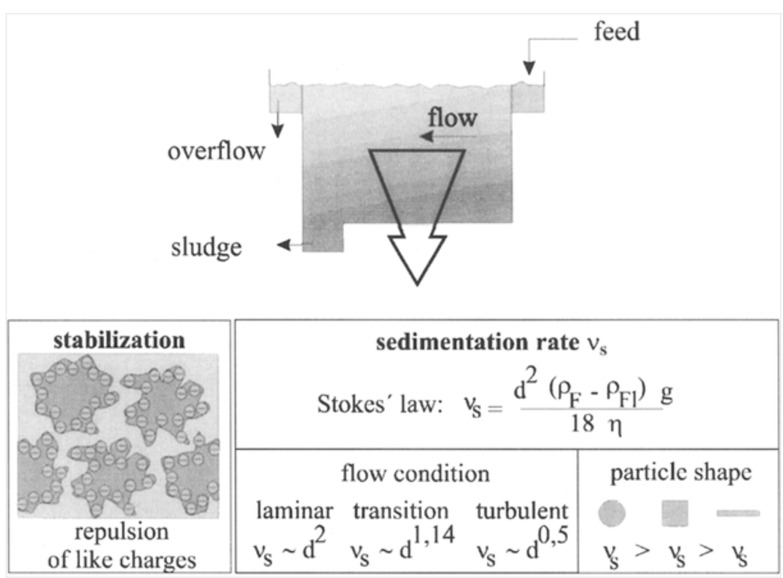

Fig. 1 Schematic representation of the dependence of sedimentation rate upon particle size, particle shape and flow condition in a simple horizontal flow apparatus

which closely simulates the practical conditions. This apparatus enables various flocculating agents to be compared and their optimum concentrations to be determined [12]. As far back as 1993, this apparatus was used to establish the range and doses of flocculating agents for the large-scale industrial plant for mechanically separating port sediment METHA (**Me**chanische **T**rennung von **Ha**fenbaggergut) in Hamburg harbor [13, 14].

The aim of this study is to show, using selected effluents, that in special cases results can be transferred, and that optimum dosage rates can be predicted on the basis of flocculation and dewatering experiments in conjunction with electrokinetic measurements depending on the flocculation model. In addition, an attempt will be made to devise models taking into account real macromolecular structures.

Experimental

Slurries investigated

Four slurries from different sources were available for investigation: port sediment from dredging the navigation channels of the River Elbe, sugar beet washings from a sugar factory, sewage sludge from the Köhlbrandhöft sewage works in Hamburg and an aluminum hydroxide suspension as an example of an industrial slurry from the production of offset printing plates.

Port sediment

The port sediment from Hamburg harbor is generated during the maintenance of the shipping channels for navigation. The natural suspended particles conveyed in the water of the River Elbe settle in the harbour area because of the low flow rate caused by the tide. Every year approximately 2.5 million m^3 of dredged material are extracted, which since 1993 have been separated into sand and sediment fractions in industrial separation plant METHA. Dewatering is carried out on belt screen presses followed by high-pressure rams to a content of at least 55% total solids (TS).

Sugar beet washings

The water which contains earth is generated in the sugar factory when the trucks are sprayed during unloading of the sugar beets from the trucks, during the hydraulic transport to the storage and processing areas, and during the intense cleaning operation before processing. The slurry that accumulates at the bottom of a sedimentation basin has a total solids content of approx. 12%. It is conditioned with an anionic flocculating agent and dewatered in centrifuges to 45% total solids.

Sewage sludge

The sewage sludge originates from the Köhlbrandhöft sewage works in Hamburg. Coarse solids and the accompanying sand are mechanically removed from the raw effluent in a sedimentation basin. The subsequent biological cleansing stage, which uses bacteria, produces activated sludge. A further sludge containing bacteria occurs during nitrification. The sediments occurring in the primary clarification stage, the biological cleansing stage and nitrification form the raw sludge, which then undergoes treatment in digestion towers for 28 days to produce the actual sewage sludge with an organic content of approx. 55% and 3% total solids. This is followed by flocculation with a polycation and centrifugation to give 22% total solids. The content of total solids is then increased to 55% in a drying plant heated by biogas.

Aluminum hydroxide slurry

This effluent is generated during the preliminary treatment of litho-aluminum for offset printing. To enable the aluminum to function flawlessly as a carrier for the light-sensitive coating, the aluminum oxide must first be removed with a caustic solution and then its surface roughened by acids. The main product of neutralization is aluminum hydroxide with a positive surface charge. It is dewatered in belt screen presses from a content of 1% total solids to approx. 15%.

Table 3 summarizes the data for the slurries.

Flocculation additives

The same high-molar-mass cationic flocculating agent, K1, was used in the flocculation and dewatering experiments for all four slurries, namely of the poly(acrylamide-co-N,N,N-trimethylammoniumethyl-acrylate chloride)-type (PTAC) [15], which has proven to be effective for all the slurries. Similarly, the same high-molar-mass anionic flocculating agent, A1, was used: of the polyacrylamide-co-acrylate-type (PAA-PAAm) [16].

For the flocculation and dewatering experiments combined with the electrokinetic measurements two cationic poly(diallyldimethylammonium chloride) samples (PD) of different molar mass were used (PD1 low molar mass, PD3

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Table 3 Overview of the data for the slurries (PS = port sedimet, SS = sewage sludge, AH = aluminum hydroxide suspension, BW = beet washings; TS = content of total solids)

Parameter	PS	SS	AH	BW
TS, %	6	3.2	1	12.5
Loss of ignition, %	17	52	(*)	13.5
Ratio in dry substance of inorganic:organic	83:17	42:52	100:0	86.5:13.5
Zeta potential, mV	− 25	− 28	+ 3.5	− 26
Particle size distribution, μm	1 … 1000	1 … 200		1 … 200
Mean particle size, μm	16	23	> 2**	13
Salt content of TS, %	< 1	< 2	60 … 70	< 1
Main mineral component	clay minerals		$Al(OH)_3$	clay minerals

* The loss on ignition is mainly caused by the expulsion of water.
** Figures provided by manufacturer of offset printing plates.

Table 4 Data for the flocculating agents employed. ($[\eta]$ = Staudinger Index, M_W = weight-average molar mass, CD = charge density, d = coil diameter, c^* = critical concentration)

Code	Substance group	$[\eta]$ ml/g	M_W 10^3 g/mol	$[\eta]$-M_W relationship	CD%	d μm	c^*%
K1	PTAC	1160	12900	$[\eta] = 6.62 \cdot 10^{-3} \cdot M_W^{0.83}$ [15]	55	0.26	0.22
A1	PAA-PAAm	3400	7600	$[\eta] = 3.90 \cdot 10^{-4} \cdot M_W^{0.91}$ [16]	36	0.32	0.07
PD1	PD	13	5	$[\eta] = 4.83 \cdot 10^{-3} \cdot M_W^{0.88}$ [17]	100	0.004	19.23
PD3	PD	305	411	$[\eta] = 4.83 \cdot 10^{-3} \cdot M_W^{0.88}$ [17]	100	0.054	0.82

high molar mass) [17]. The molecular parameters are shown in Table 4.

Flocculation and dewatering apparatus

A special piece of apparatus was developed at Hamburg University for determining the effectiveness of flocculation additives (FA) and for measuring their optimum dosage rate. The patented computer-assisted flocculation and dewatering apparatus (FDA) works with a high degree of reproducibility and is portable [12].

This apparatus enables the slurry to be conditioned with a precisely measured dose of flocculating agent. The degree of mixing required for flocculation is achieved by stirring, and the slurry is then filtered with compressed air, with the filtrate being collected on a balance. The evaluation unit is connected to the balance and records the mass of filtrate as a function of time. The FDA has proven its worth for slurries with a total solids content (TS) of greater than 0.4% (by adjusting the measuring conditions it is also possible to measure below this figure).

The requirement made on the flocculating agent in the actual process is that the particles agglomerate to produce sufficiently large and mechanically stable flocs. The better the criterion is fulfilled, the easier it is to extract the water, i.e., the steeper the gradient of filtrate mass against time will be (filtration curve), approaching a limiting value at high filtrate yield. The latter refers to the maximum quantity of water that can theoretically be separated. Figure 2 shows various filtration curves obtained from port sediment under different flocculation modes [13]. Monoflocculation involves the addition of a single additive, in dual flocculation two oppositely charged flocculating agents are added one after the other (1) addition, stirring, 2) addition, stirring).

The apparatus achieves a particularly high level of practical relevance due to the fact that it covers the technically important time interval of a few minutes, for example the time that the flocculated sludge spends in the straining zone of a belt screen press. Even the dewatering behavior in the first minute – in comparison with the unconditioned system – allows deductions to be made about the suitability of the flocculating agent in the real process. Parker was able to demonstrate the aptness of this laboratory apparatus as a simulation for a large-scale industrial plant in optimization studies for the FA-dosing program at METHA [13, 14], where dewatering of the flocculated harbor sediment was carried out on belt screen presses with a sieve width of 3.5 m.

Fiber-optic flocculation sensor

This apparatus developed and kindly provided by BASF, Ludwigshafen, enabled the optimum FA-dosage

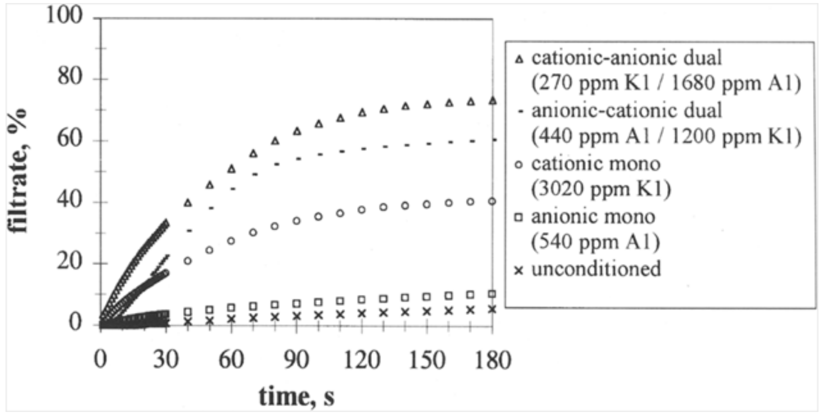


Fig. 2 Optimal filtration curves of port sediment in mono and dual flocculation [13]

concentration to be determined by measuring the floc size in a flowing medium [18–20]. The thinking behind this measuring technique is that the degree to which the slurry can be dewatered increases as the dimensions of the flocs grow. The measure for the floc size is a so-called F-value (a dimensionless number between 0 and 10). Comparative investigations between the fiber-optic flocculation sensor and the flocculation and dewatering apparatus with a large number of flocculating additives of differing molar masses and chemical nature exhibited an outstanding level of agreement in determining the optimal dosage concentration, i.e., the maximum size of flocs (highest F-value achieved) and the optimum level of dewatering were obtained with the same FA-dosage.

However, when comparing the different FA's, differences did occur depending on the molar mass, expressed here by the Staudinger Index $[\eta]$. For clarification the maximum F-values obtained with some FA's are compared with so-called dewatering indices I_E (Fig. 3). A dewatering index, I_E, reduces the large amount of data in a filtration curve to a dimensionless numerical value between 0 and 100, and thus makes rapid interpretation possible [21]. It is obtained from the arithmetic mean of all the filtration values divided by the number of filtration values, and is only of use where the same measuring conditions pertain. A small I_E indicates a poor dewatering capacity, and a large I_E a good dewatering capacity.

As Fig. 3 shows, there is good degree of correlation between dewatering capacity and floc size at small Staudinger indices. At the larger Staudinger indices, above approximately 300 ml/g, i.e., towards increasing molar masses, there is a large discrepancy between these values, irrespective of the chemical nature: the dewatering capacity tends towards optimal values, whereas the floc size stagnates. This means that, according to the measurements in the fiber optic flocculation sensor, in some cases the high molar mass FA's form smaller flocs than the low molar

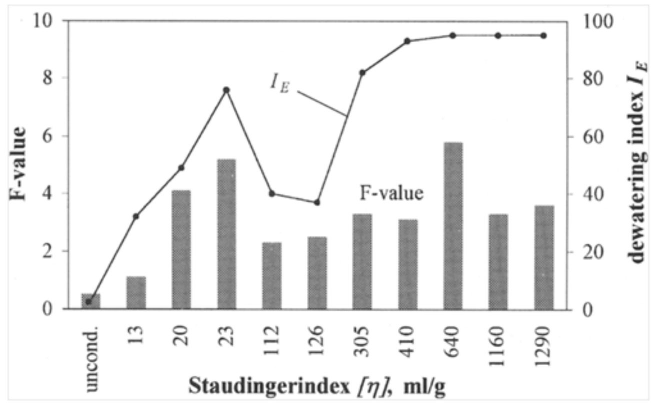


Fig. 3 Plot of F-value (measure of the floc size in the fiber-optic flocculation sensor) and dewatering index I_E (measure of the dewatering capacity in the flocculation and dewatering apparatus) against the Staudinger index $[\eta]$ of different flocculation additives

mass additives. This contradicts both the visual evidence, according to which the high molar mass FA's form distinctly larger flocs, and the agreement with the best dewatering capacity.

It remains unclear as to what extent the floc size is influenced by the shear stress in the flow profile of the tubes in the fiber-optic sensor.

For this reason and because of the good experience with port sediment the practically relevant experiments in this study were conducted with the flocculation and dewatering apparatus.

Results and discussion of the flocculation and dewatering experiments

In the investigation of port sediment it was shown that, despite a negative zeta potential, conditioning can be carried out with both polycations and polyanions, although the latter are less effective. The combined application of polyanions and polycations, termed dual flocculation, has proven to be more effective than the use of a single polyelectrolyte (monoflocculation). The two addition sequences are not equal: the cationic–anionic method is more effective for port sediment than the anionic–cationic (see Fig. 2). Originally, in the laboratory experiments, the optimum method was found to consist of carrying out the dual method twice successively (double-dual procedure) [13, 14]. In practice at METHA a three-stage separation strategy proved to be sufficient (optimized dual procedure): a low-dosage cationic–anionic dual flocculation for preliminary thickening (from 6 to approx. 18% TS) is followed by a cationic monoflocculation of the sediment. Introduction of the optimized dual procedure enabled the efficiency of dewatering to be significantly improved while both ensuring a shear strength of 20 kN/m^2 for the dewatered sediment and achieving a 10% saving on polyelectrolyte.

This optimized dosing strategy is the result of a time-consuming series of experiments. To enable future work on unknown systems to proceed more purposefully, the dewatering behavior of all four slurries was investigated and correlated with their parameters.

The following presents selected results from all four of the slurry samples illustrated by optimal filtration curves.

The port sediment and the sugar beet washings exhibit an approximately analogous behavior (Figs. 2 and 4): in both sludges with a negative particle charge the dewatering capacity was significantly improved with the cationic and FA K1, and still moderately improved with the anionic FA A1. Dual flocculation is in fact clearly superior to monoflocculation for the port sediment, which is not the case for sugar beet washings, but in both sludges the FA doses can be reduced by approximately 1/3 when the dual procedure is employed. There is a difference in the effectiveness of the anionic–cationic dual procedure, which is not very effective for sugar beet washings, but in the case of port sediment even surpasses cationic monoflocculation.

Table 3 also shows the agreement between the two slurries in terms of their sludge characteristics, with the zeta potential, the loss on ignition and mineralogical composition (clay minerals) being of importance.

In contrast, a significant improvement in the dewatering capacity for sewage sludge (Fig. 5) can only be

Fig. 4 Optimal filtration curves for sugar beet washings

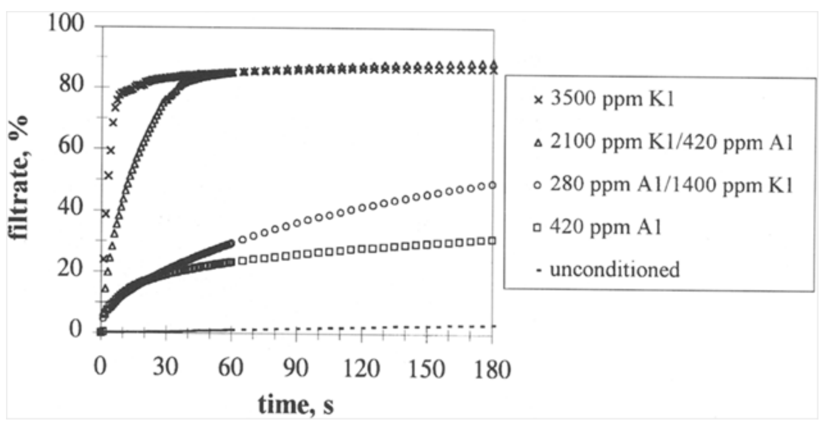
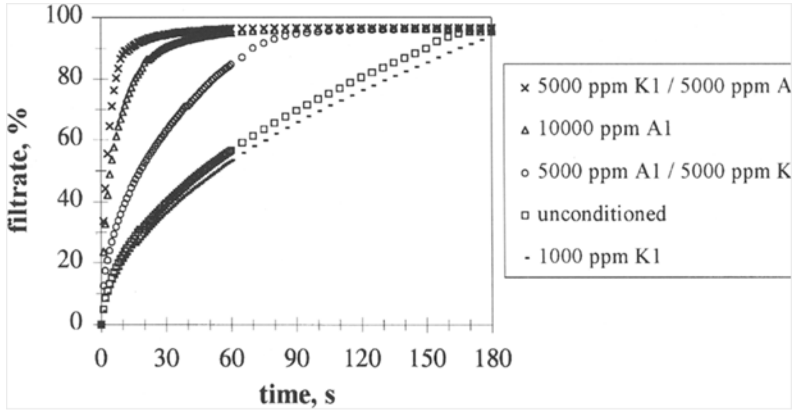


Fig. 5 Optimal filtration curves for sewage sludge (diluted to 0.4% TS)*



*The original sludge was diluted to 0.4% TS with mains water so as to approximate the conditions of the electrokinetic experiments, in which dilution to 0.04% TS occurred due to the measuring technique. Dewatering experiments on sewage sludge with 0.04% TS were not possible

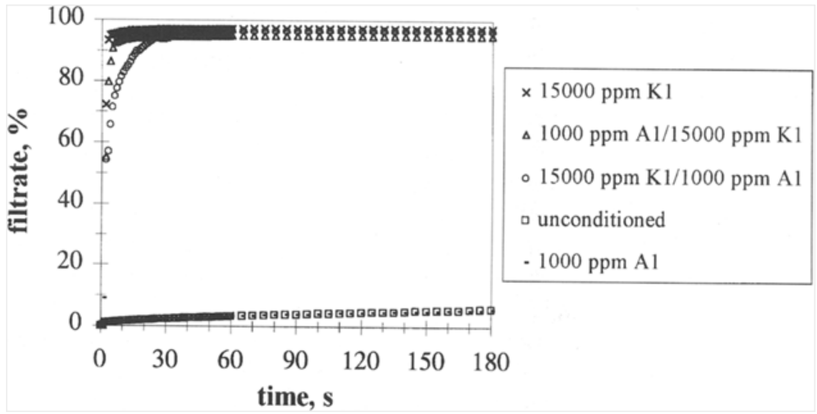


Fig. 6 Optimal filtration curves for the aluminum hydroxide slurry

observed with the cationic FA, the anionic additive does not prove to be effective. No synergetic effect occurs in dual flocculation, i.e., the dewatering capacity cannot be increased compared with monoflocculation or the required quantities cannot be reduced. The dosage rates are worthy of note since they are higher by a factor of 5 than those required for port sediment and sugar beet washings. These discrepancies in the behavior of sewage sludge can presumably be attributed to the high biological organic component.

The aluminum hydroxide suspension as an example of a slurry with a positive particle charge (Fig. 6) can be dewatered very successfully with the anionic A1; on the other hand results with the cationic K1 are worse than for the unconditioned slurry. In cationic–anionic dual flocculation although it is not possible to reduce the total dosage, the dewatering capacity can be somewhat improved in comparison with monoflocculation. In contrast, anionic–cationic variant is significantly worse.

The high final values of the filtrate yield of approximately 97% for sewage sludge and aluminum hydroxide suspension can be attributed to the low TS content. The higher TS contents of port sediment and sugar beet washings mean that more capillary water is retained in the filter cake.

To summarize, it can be stated that slurries with similar characters do resemble each other in relation to their properties in monoflocculation and dual flocculation. Where properties differ, they react with unpredictable differences, particularly as far as optimal dosage rates and behavior during dual flocculation are concerned.

Prediction of FA dosage by means of electrokinetic investigations

Through a combination of zeta and streaming potential measurements Kötz et al. succeeded for the first time in detecting interactions between suspended particles and polyelectrolytes, which allowed conclusions to be drawn about flocculation mechanisms [22]. It was possible to successfully correlate these conclusions with the dewatering experiments using the flocculation and dewatering apparatus [23]. It thus became possible for the first time to make predictions about the required dosage of flocculating additives while taking into account flocculation models.

By means of two selected examples it will be shown how, in principle, measurements of zeta and streaming potential, dewatering experiments and flocculation models can be united and used to provide guiding predictions on the FA doses required.

First of all an outline will be given of the two flocculation models [10, 24]:

Patch charge model

Polyelectrolytes with small to medium molar masses adsorb on the surface of the particle so that there are areas with negative and positive charges. The particles arrange themselves in accordance with electrostatics and form mechanically less stable flocs, the cohesion of which is greatest when the charge is neutralized.

Bridging model

Polyelectrolyte of sufficiently high molar mass are adsorbed onto two or more particles in a bridging manner and form aggregates that are relatively mechanically stable. The surface neutralization of these aggregates requires fewer polycations than for the individual particles.

In [22] detailed derivation is given to support the assumption that the flocculation of sewage sludge with PD1 involves a patch charge mechanism and a bridging mechanism with PD3.

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Table 5 Quantities of PD required for neutralization of the surface charge (zeta potential $\zeta = 0$) and for the zeroing of the streaming potential ($U = 0$) in cationic monoflocculation

Sample	c(PD) in ppm for $\zeta = 0$	c(PD) in ppm for $U = 0$
PD1	51 500	51 900
PD3	17 000	25 750

Table 5 shows the quantities of PD required for the zeta and streaming potential to pass through zero ($\zeta = 0$ and $U = 0$) in sewage sludge with a TS content of 0.4%. Figures 7 and 8 show the corresponding filtration curves with the flocculating additives PD1 and PD3.

With the low molar mass PD1 there is agreement between the dosage rates for the zeta potential to pass through zero (complete compensation of the surface charge) and streaming potential and the optimal dewatering capacity. This correlates with the theoretical expectations for the patch charge mechanism, which is generally assumed for low molar mass polyelectrolytes.

With the higher molar mass PD3 the FA requirement for good dewatering capacity is significantly lower compared with the PD1. This can be explained by the ability of long-chained molecules to rapidly form links between sewage sludge particles so as to produce aggregates with a lower total surface area, which thus require fewer polycations for neutralization of the surface charge (in this case 17 000 ppm instead of 51 500 ppm with PD1, Table 5). The higher consumption to achieve zero streaming potential is an indication of the sensitivity of these aggregates to shear, i.e., partial destruction of the aggregates due to the measuring technique results in a renewed increase of the cation requirement for surface neutralization. A patch charge mechanism can be ruled out for this sample because, according to Fig. 8, optimal dewatering capacity has already been achieved before the surface charge of the aggregates has been neutralized. A bridging mechanism can therefore be assumed for the flocculation of these aggregates [22, 23].

In the case of the patch charge mechanism predictions are simple and accurate. For the higher molar mass flocculation additives, where the bridging mechanism is of

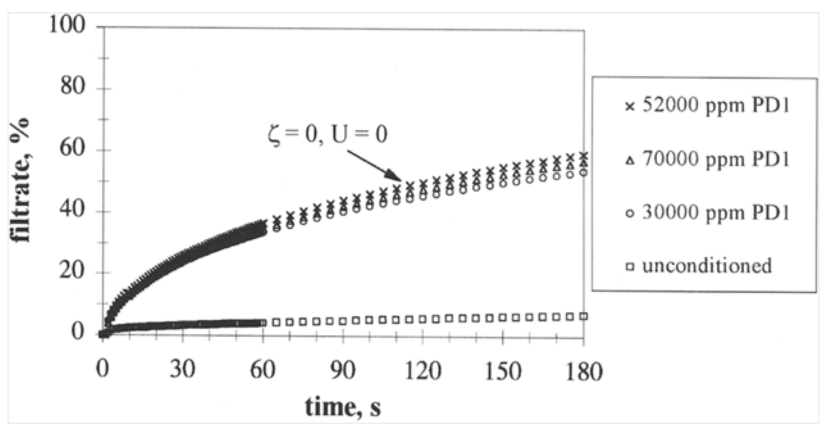

Fig. 7 Filtration curves of sewage sludge with the poly(diallyldimethylammonium chloride) sample PD1

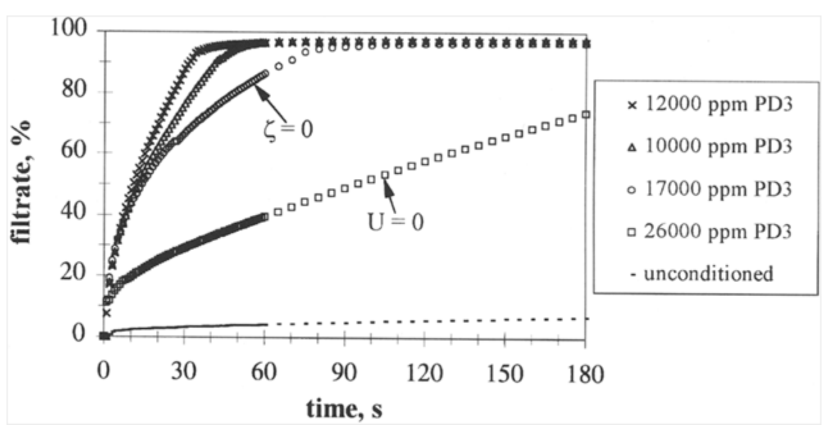

Fig. 8 Filtration curves of sewage sludge with the poly(diallyldimethylammonium chloride) sample PD3

importance, exact predictions cannot be made but guiding estimates are possible.

Proposed models for flocculation mechanisms

The classical polymerisates, to which polyacrylamide and its derivatives belong, are present as coils in solution. As shown by Table 4, the coil diameter of the FA used here does not exceed 0.3 μm. The mean particle diameter of the slurries employed is approximately 20 μm. Even the largest FA coils are therefore at least a factor of 60 smaller than the mean suspended particle.

A bridging mechanism as is often shown in drawings in the form of snake-like threads, weaving from particle to particle [10, 24], is unrealistic from the macromolecular point of view.

Every polymer coil can be assigned a volume ratio, expressed by the Staudinger index $[\eta]$, which can for example be obtained by viscosimetry [25]. According to the Mark-Houwink $[\eta]$-M_w-relationship the following proportionality exists between the Staudinger index $[\eta]$ and weight-average molar mass M_w:

$$[\eta] \sim M_w^{0.5\ldots2} . \qquad (1)$$

The exponent varies, according to the polymer–solvent system and temperature, from 0.5 (pseudoideal, theta conditions) to 2 (maximum expanded coils like a rigid rod). For these polymers exponents in the range from 0.6 to 1 are found. From the exponents, which for the FA used here are smaller than 1 (partially expanded coil), it follows that the coil density decreases as the molar mass increases.

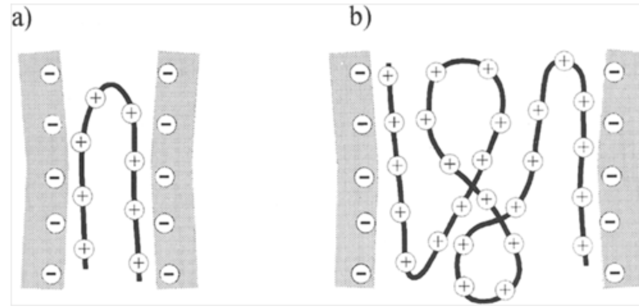

Fig. 9 Schematic flocculation mechanisms with short-chained flocculation additives (a) and long-chained additives (b)

The modified model proposed here is aimed as an approach for explaining the different findings for low and high molar mass FA in terms of the coil density instead of the chain length: the low molar mass FA coils are so small and dense that all the charge-bearing groups can be neutralized by the surface charges of two adjacent particles. The repulsive action of the like surface charge is reduced and the distance between particles diminishes. From this, in agreement with the patch charge theory, it follows that optimum flocculation and dewatering capacity are achieved when the charge is completely compensated (Fig. 9a).

In high molar mass FA coils the density is so low that it is not sterically possible for all charge-bearing groups to be neutralized with one surface charge. Despite uncompensated surface charges the flocs are stable, since the large FA coils mean that the particles do not lie so close together that Coulombic repulsion can gain the upper hand (Fig. 9b).

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