



MECHANISMS OF FLOC FORMATION IN SLUDGE CONDITIONING WITH POLYMERS

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ABSTRACT

In flocculation of dilute suspensions a period of slow mixing is necessary to increase the probability of particle collisions that are necessary for flocculation to occur. When flocculating sludges, the collision frequency is so high that flocs are formed immediately after rapid mixing. However, controlled mixing of the flocculated sludge for some time period does improve dewaterability. The mechanisms that are involved have been studied in detail and the subject of this paper. The results show that after rapid mixing and initial floc formation there might still be polymer in solution, depending on polymer dose. Prolonged mixing results in breakage of large aggregates and in particle/floc surfaces that are not yet covered with polymers. Subsequently the excess polymer adsorbs onto these surfaces. From changes in sludge rheology one can see that within a period of about one half to one minute the bulk properties change dramatically. After the initial floc formation the suspension is in a state characterized by a three-dimensional network structure with strongly interacting, voluminous flocs. After the mixing period there are more discrete and less interacting flocs. Especially the properties of the filter cake from pressure filtration are then more favorable.

KEYWORDS

sludge conditioning; flocculation; polymers; floc formation; floc network; charge concentration; gravity drainage; cake solids content.

INTRODUCTION

It has been shown that in conditioning of sewage sludges with polymers flocs are forming immediately after dispersion of the polymer (Langer and Klute, 1993). Rapid mixing of the sludge and polymer with high intensity during a period of one second resulted in a rapidly dewatering sludge. Due to the high particle concentration in sludges the adsorption of molecules onto particle surfaces and the flocculation of the particles can obviously be accomplished within seconds. However, from batch-type experiments it has been established that an optimum mixing time exists, which is dependent on mixing intensity (Werle et al., 1984) and polymer dose (Novak et al., 1988). The optimum mixing time can last up to three minutes (Werle et al. 1984). Other investigations yielded an optimum mixing time of two minutes, which was interpreted as the period necessary for a process the author called floc maturing (Sander, 1980).

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According to Novak *et al.* (1988) the mixing in biological flocs might be required to break large bioflocs, so that excess polymer can react. So far, exactly what occurs in a polymer flocculated suspension when improving its dewaterability during an extended mixing period has not been examined in detail.

In the process of polymer flocculation several steps have to be considered. Besides the mixing, adsorption and flocculation steps a re-arrangement of the adsorbed polymer chains is occurring (Gregory, 1988). The macromolecules adsorb initially with only a few segments on particle surfaces forming loops and tails until finally a more flat conformation is attained. In dilute suspensions, this reformation of the adsorbed polymer usually takes place before collisions between particles and thus flocculation occurs. Since in sludges the collision probability is very high and a rapid flocculation is observed, there are certainly conformational changes of the adsorbed polymer chains after the flocculation step. One can imagine that the polymers adsorbed at the surfaces of the flocs will change with mixing time to a flat conformation. But also the polymer molecules that are located within the floc might change their conformation. Under certain, especially hydrodynamic, conditions this can lead to a densification and strengthening of the floc (Higashitani and Kubota, 1987; Mühle and Domasch, 1991). It can thus be concluded that changes in the conformation of the adsorbed polymers are in some way responsible for the improvement in dewaterability of polymer conditioned sludges during a fixed period of mixing.

EXPERIMENTAL MATERIALS AND METHODS

Materials

The experiments were performed with anaerobically stabilized sludges from municipal wastewater treatment plants (WWTP). The sludge used in the batch experiments is taken from the Albtal WWTP (28 g/L total solids, 51% volatile solids) and the Berghausen WWTP (34 g/L and 45 %, resp.). The other data presented here are from experiments with sludge from Berghausen, which had then 50 g/L total and 30 % volatile solids. The polymers used were commercial cationic polyelectrolytes (M.W. 6 mio.) from Stockhausen Co., Germany. The polymer products were chosen identically to the ones applied in full scale operation at the respective WWTP, that is *Praestol 650 BC* (40-45 % ionic; 2.41 meq/g) for sludge from Albtal WWTP and *Praestol BC 655* (70-80 %; 4.15 meq/g) for sludge from Berghausen WWTP.

Methods

The specific resistance to filtration (SRF) was determined from gravity filtration. For each filtrate volume increment ΔV per time increment Δt one value SRF_i could be calculated by setting the pressure difference equal to the hydrostatic pressure in the sludge container (the media resistance had been determined in advance). During the period of cake formation the mean of the SRF_i was calculated and represents the SRF from "no-pressure" filtration. For the determination of the cake solids, a pressure filtration (6×10^5 Pa) was performed using a piston in the pressure cell so that no gas/slurry interface existed and the sample could drain in two directions (through bottom and piston).

The charge concentration was determined by charge titration and identification of the isoelectric point. Solutions of polyelectrolyte of known normality (cationic Poly-DADMAC; PPVS, anionic standard) were titrated into the sample, while the streaming current potential was measured by a charge detector.

The mean floc size was determined from photographs taken through a window that had been integrated in the pilot plant. The flash was mounted under a 45° angle so that shadows and floc contours could be identified on the photographs. The pictures were digitized, enhanced and smoothed by use of an image-processing software. Line maps were drawn and from the distribution of the gray-scales along these line the flocs could be identified. Thus, an estimation of the mean floc size was obtained avoiding sampling and dilution of the sample.

DESCRIPTION OF THE QUALITATIVE MODEL

The following model is based on experimental work on the conditioning of anaerobically stabilized sewage sludges with polymers. Besides the evaluation of the conditioning process by the dewatering characteristics of the sludge, attention has been paid to other bulk properties, namely the rheology of the suspension and the quality of the filtrate. Results will be discussed in the next section on the basis of the model described below.

After dispersion of the polymer in the sludge, the following states of aggregation have been identified. With sustained mixing of the flocculated suspension, there is a steady transition from phase I to ultimately phase IV. How long the different phases will last is depending on numerous parameters of the conditioning process such as polymer dose, mixing intensity and sludge properties.

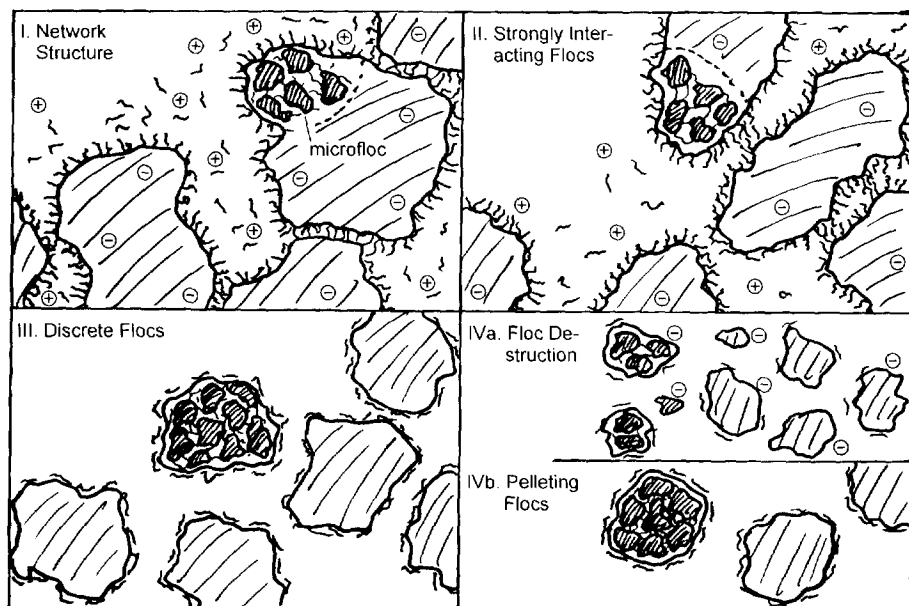


Fig. 1: Schematic of the different states of aggregation during the process of sludge conditioning with polymers; depending on floc strength and applied shear the ultimate state will be either IVa or IV b

Phase I "Network Structure": This state of aggregation is characterized by a three-dimensional network structure. The flocs are linked by polymer bridges to form an elastic network. At high polymer doses there is still excess polymer in solution. It cannot adsorb onto the surfaces of the bulky flocs for presumably steric reasons. Inside the voluminous flocs particles are trapped that are insufficiently dehydrated by polymers. This is indicated in Fig. 1 by the negative charges inside the flocs.

Phase II "Strongly Interacting Flocs": After a decay of the network structure due to mixing, a movement of the flocs relative to each other is now possible. The bulk suspension does not react as an elastic solid anymore but there are still three-dimensional structures due to strong interaction between the flocs. This high degree of interaction results from the polymer-covered surfaces of the flocs. It is believed that the polymers which are adsorbed at surfaces on the outside of the flocs are forming loops and tails.

Depending on the polymer dose there might be polymer in solution. This polymer will react when the bulky flocs are broken down by shear and unsaturated particle surfaces get accessible.

Phase III "Discrete Flocs": The voluminous flocs have been broken down to smaller units and all of the polymer is consumed. There is now a more flat conformation of the polymer at the floc surfaces so there is less interaction between the polymer layers of two adjacent flocs. Probably there is also an inner contraction of the floc and thus a reduction in floc size.

Phase IVa "Floc Destruction": Prolonged mixing and shear might lead to floc destruction. Since there is no more active polymer the breakage of flocs is irreversible. An erosion of primary particles from the surfaces of these floc segments is possible.

Phase IVb "Pelleting Floc": When the shear resistance of the flocs is high, relative to the shear stress resulting from mixing, a floc destruction will not take place. Under suitable hydrodynamic conditions there will be a contraction and densification of the floc by exudation of water from inside the floc (Yusa, 1977). The floc size decreases and the flocs are of almost spherical shape.

EXPERIMENTAL DATA SUPPORTING THE MODEL

Results from batch-experiments

Rheological Properties of the Flocculated Sludge. Wastewater sludges such as anaerobically stabilized biological sludges can be regarded as concentrated suspensions. The volume fraction of the solids may be as low as 3-6%, but since these sludges are electrostatically stabilized with an extended double layer surrounding the particles, their effective volume fraction is much higher. The double layer is also responsible for a soft interaction between the particles resulting in viscoelastic flow behavior (Tadros, 1985). In concentrated suspensions the bulk properties of the suspension are dominated by the interparticle interactions. These interactions are dependent on the state of aggregation and change dramatically when polymer solution is added. This is exemplified in Fig. 2 by plotting the torque at the stirrer shaft versus the time of mixing, beginning with the addition of the polymer.

One can see that the torque is increasing while introducing the polymer until a maximum is reached, followed by a monotonous decrease. From the torque one can calculate an apparent viscosity of the sludge, provided the relationship between Power- and Reynolds-Number for the specific stirrer/reactor system is known.

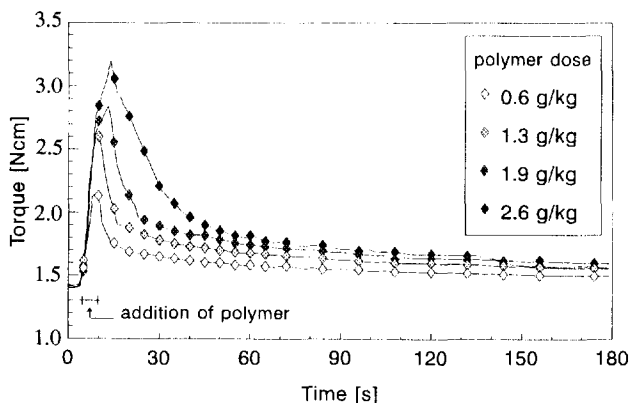


Fig.2: Torque measured at the stirrer shaft of a batch reactor (910 mL, helical ribbon screw impeller, 250 r.p.m.) during polymer addition and flocculation reaction

While the existence of this phenomenon has been documented elsewhere (Campbell and Crecuolo, 1982); it is as yet unexplained. From the work of Michaels and Bolger (1962) on the flow behavior of flocculated suspensions it is known that the energy dissipated within the suspension can be attributed to three different processes. Part of the energy is used to deform and stretch network structures and extra energy is needed to actually break bonds between flocs. In addition, viscous energy is dissipated by the fluid flowing around the flocs. These findings are also described and quantified by the elastic floc model of Firth and Hunter (1976). Otsubo and Umeya (1984) showed that bridging of particles in polyacrylamide solutions resulted in an increase in apparent viscosity. A network structure due to a percolating floc showed clearly a solid-like elastic behavior (Otsubo, 1990).

It seems likely that the observed increase in apparent viscosity (Fig. 2) is due to the existence of an elastic floc network. The high energy dissipation after polymer addition can then be attributed to an elastic deformation of the floc network, while the peak indicates the point where the network bonds rupture. The interaction between the flow units (flocs) is then continuously decreasing, resulting in a decrease in energy dissipation. The strength of the network bonds and thus the energy needed to rupture these bonds is higher the more polymer is added to the sludge (Fig. 2). One can also see that the steady-state apparent viscosity of the flocculated sludge is higher than the viscosity of the electrostatically stabilized sludge. In Fig. 3 the four different states of aggregation as described above are roughly related to the apparent viscosity of the sludge (represented by the torque).

Apparent Viscosity and Filterability. In order to relate the dewatering behavior to the flow properties of the flocculated sludge the following experiment has been set up. The dosing of the polymer solution and the rapid mixing has been accomplished in the pilot plant, using an in-line cylinder mixer at 1000 r.p.m. as described in an earlier paper (Langer and Klute, 1993). Immediately after the rapid mixing the sludge was passed into a batch reactor until it was entirely filled. The flocculated sludge was now stirred at 150 r.p.m. for up to 5 minutes while the torque was recorded (see Fig. 3). The experiment was repeated several times but the periods of mixing in the batch reactor were varied. Samples were taken and analysed by gravity drainage and pressure filtration. The existence of an optimum mixing time with regard to the SRF is demonstrated in Fig. 4. It coincides with the point in Fig. 3 where the apparent viscosity is approaching its steady-state value. While the SRF is deteriorating the solids content of filter cake from pressure filtration is steadily improving. Thus, along with the changes in rheological properties (Fig. 3) there is also a variation in the dewatering characteristics of the sludge (Fig. 4). In the example discussed a mixing time of about ½ minute improved the filtration behavior (SRF) of the sludge as well as solids content in the dewatered filter cake significantly compared to the sample taken immediately after rapid-mixing.

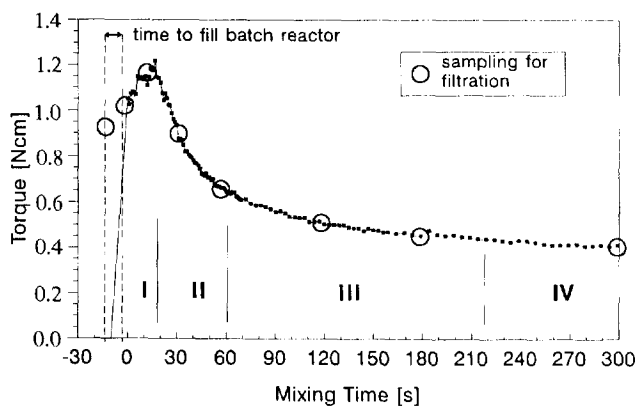


Fig. 3: Torque measured while stirring the flocculated sludge (polymer dose 4.4 g/kg) in a batch reactor (910 mL; helical ribbon screw impeller); the roman numerals refer to the schematics in Fig. 1

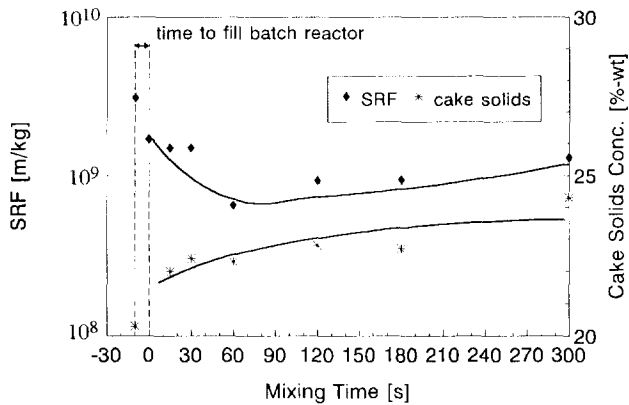


Fig 4: Specific resistance to filtration from gravity drainage and cake solids content from pressure filtration vs. time of mixing in a batch reactor, the data correspond to Fig. 3

Results from pilot-plant experiments

After polymer addition and dispersion the flocculated sludge was now passed through a mixing reactor with paddles and baffles and a detention time of 30 seconds. This reactor did have little longitudinal mixing (length:diameter=7.5) and was mounted horizontally to avoid sedimentation.

Charge concentration in the filtrate. The filtrate from gravity drainage was taken for the determination of the charge concentration. Additionally, in some samples the charge concentration in the sludge supernatant was determined. A comparison of the two results revealed no differences as long as the sample contained a surplus of negative charges, indicating unflocculated colloidal material. When there was excess polymer in the solution phase of the flocculated sludge, the filtrate contained less positive charges than the supernatant. Obviously a part of this polymer was retained when passing through the filter cake and filter medium. This has to be considered when evaluating the data in Fig. 5.

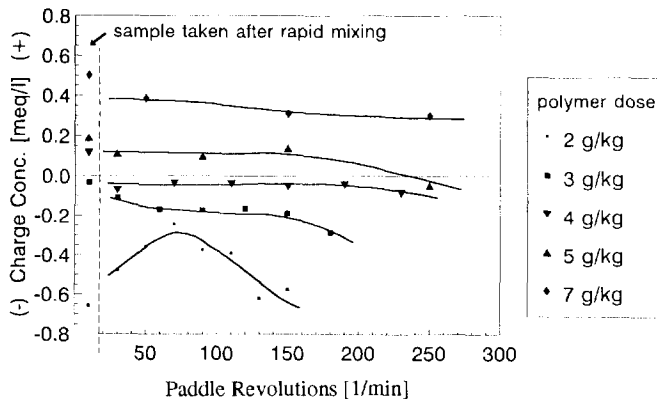


Fig. 5: Charge concentration in the filtrate from gravity drainage at different polymer doses as a function of mixing intensity in the flocculation reactor

The results show that for polymer doses of 4 g/kg and above the samples taken directly after rapid-mixing did reveal a surplus of positive charges in the filtrate. The concentration of the excess polymer decreases while the sludge passes through the mixing reactor (polymer dose 5 and 7 g/kg) and even a charge reversal in the filtrate could be observed (dose 4 g/kg). Also, an increase in mixing intensity can result in

a charge reversal (dose 5 g/kg). Breakage of flocs and subsequent erosion of primary particles leads to either consumption of polymer in solution and thus a reduction of the positive charges in the liquid phase or to an increase in negative charges, if no active polymer is present. An exception is the underdosed system (2 g/kg), where moderate mixing does reduce negative charges in the filtrate.

A titration of the raw sludge with the same polymer that was used as flocculant in the above experiment yielded a very high polymer dose (13 g/kg) in order to attain the isoelectric point. It can thus be concluded that a complete charge neutralisation is never attained (and obviously not necessary) in regular conditioning operation. During the titration the sludge sample was continuously subjected to high shear in a narrow gap (900 μm) between the container wall and the oscillating piston for a period of about 15 minutes. It can therefore be concluded that in sludge conditioning with polymers the flocculant dose necessary for charge neutralisation is strongly dependent on the applied shear.

Specific resistance to filtration. Mixing the flocculated sludge for 30 seconds in the flocculation reactor could improve the filterability for all polymer doses (Fig. 6). However, if the mixing intensity was too high the SRF was increasing. The lower the polymer dose, the more sensitive are the flocs to shear and the more narrow is the region of optimum mixing intensity. At the polymer dose 5 g/kg the mixing intensity had little effect on the drainability of the sludge.

Assuming that the sludge samples taken after rapid mixing consisted of a floc network (phase I) it can be concluded that this state does not have optimum dewatering behavior. At least in the optimum dosing range (3 to 5 g/kg) the SRF is lowest when discrete flocs are forming (phase II and III). Excess mixing results in floc destruction (phase IVa) and an increase in SRF. If the polymer dose was as high as 7 g/kg the drainability was poor. However, the SRF values are calculated based on the assumption that the filtrate viscosity is equal to water. This might not be true for sludges conditioned at high polymer doses, as has been shown by Christensen et. al (1993). The surplus of positive charges (Fig. 5) does indicate the existence of polymer so that a higher viscosity can be expected. This might be one of the reasons why the "phase I" sludge exhibits poor drainability.

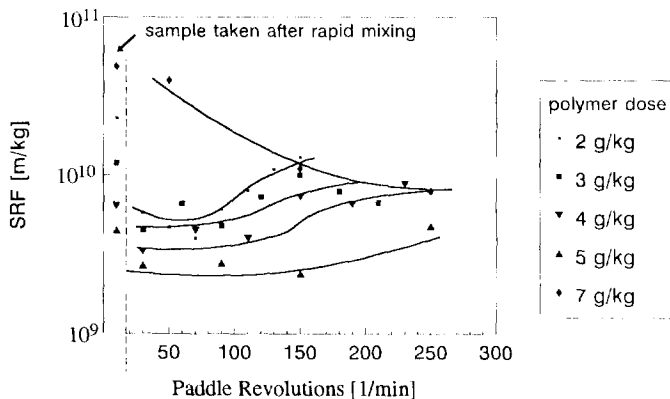


Fig. 6: Specific resistance to filtration determined from gravity filtration at different polymer doses as a function of mixing intensity in the flocculation reactor

Cake solids content. Another measure of the filterability is the attainable cake solids concentration under pressure filtration. This parameter does not provide information on how fast water is released during cake formation but shows to what extent the cake can be compressed under a fixed pressure. Fig. 7 shows that the cake solids content can be increased by several points by providing a mixing time of 30 seconds. This can be explained by the qualitative model presented in Fig. 1. If an elastic floc network exists it can be imagined that pressure filtration results in a rather compressible cake. On the other hand, if discrete and compact flocs are to be dewatered a more dense packing is possible and a cake with higher solids

content can be expected. It can also be argued that insufficiently dehydrated solids are trapped within the large and bulky flocs and consequently this bound water cannot be expressed from the flocs by pressure filtration.

A floc destruction could again be observed at low polymer doses, yielding a decrease in the cake solids content. However, if the polymer dose is high enough to produce shear resistant flocs, increasing mixing intensity results in a more favorable sludge cake. Since the floc size is decreasing only slightly (Fig. 8) there might be some compacting and strengthening effects taking place as described earlier (phase IVb).

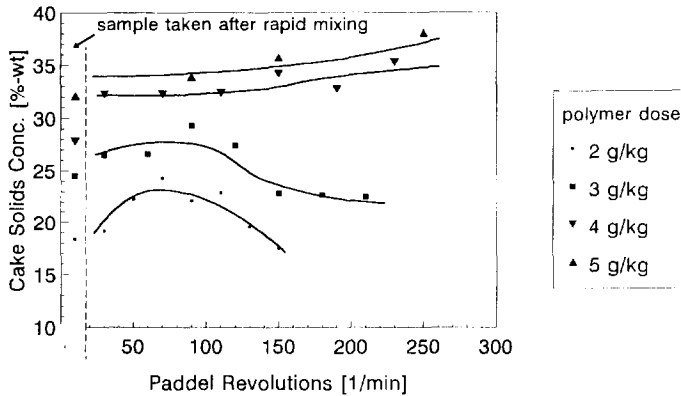


Fig. 7: Cake solids concentration after pressure filtration at different polymer doses as a function of mixing time in the flocculation reactor

Mean floc size. At a given polymer dose the largest flocs were observed immediately after rapid-mixing; the passage through a stirred reactor did result for all polymer doses in a reduction in floc size (Fig. 8). The steepest decline in floc size is observed at the lowest dose. The higher the polymer dose the more shear resistant are the flocs, as can be seen from the experiments with high mixing intensity. However, the decrease in floc size does not necessarily lead to a higher SRF, as can be seen when comparing Figs. 6 and 8. For high polymer doses there even seems to be a reverse proportionality between cake solids content and floc size (Figs. 7 and 8). The observations concerning the floc size as documented in Fig. 8 are in accordance with the conception presented above. After the dispersion of the polymer voluminous flocs are forming. As these flocs are broken down to smaller units, excess polymer in solution, so far available, can react (see Fig. 4).

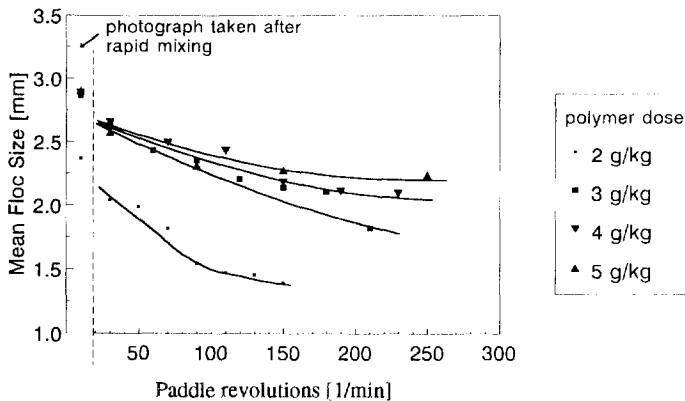


Fig. 8: Mean floc size at different polymer doses as function of mixing intensity in the flocculation reactor

OPTIMIZING CONDITIONING OPERATION

Optimal State of Flocculation

Based on the proposed model and considering the experimental results it can be concluded that a polymer-flocculated sludge has then its most favorable condition when discrete flocs rather than network structures prevail (see phase III in Fig. 1). The state characterized by a elastic floc network and bulky flocs with yet unconsumed polymer in the liquid phase has to be overcome. On the other hand, too long and too intense mixing causes floc destruction and a deterioration of sludge dewaterability. From the practical viewpoint it is of interest how long the reaction time between polymer addition and sludge dewatering has to be in order to attain optimum dewatering operation. However, the optimum reaction time is not a constant but depends on other parameters of the conditioning process.

- The higher the polymer dose, the more stable are flocs and the more energy is necessary to destroy the network structures (Fig. 2). At high doses it will take longer to achieve a complete consumption of the polymer and the desirable change in polymer conformation. Thus a longer reaction time is needed.
- The affinity between sludge particle and macromolecule (dependent on sludge properties and polymer type) also influences the mixing time requirement. A stronger flocculation reaction will require a longer time to reach the desired state for similar reasons as does a high polymer dose.
- A high mixing intensity will accelerate the network destruction, the breakage of bulky flocs and the conformational change of adsorbed polymers. The optimum state of flocculation is therefore attained faster when mixing intensity is increased.

Reactors for the Sludge Conditioning Process

Despite the numerous parameters potentially influencing the optimum mixing time the results have shown that a reaction time of 30 seconds is sufficient to overcome the network structures and improve the dewaterability. The mixing intensity did not play a very important role as long as the polymer dose was in the optimum range (4-5 g/kg). Based on pilot-plant studies on rapid-mixing (Langer and Klute, 1993) and floc formation (only part of the data could be presented here) some recommendations on reactor design for sludge conditioning with polymers are summarized in Table 1. Additional experiments showed that a 15 minutes lasting detention in a rotating drum could further improve the floc properties, yielding another increase in cake solids content after filtration. However, this positive effect could only be observed with high polymer doses (> 5 g/kg). From an economic point of view *Step 3* will be omitted.

TABLE 1: REACTORS FOR SLUDGE CONDITIONING WITH POLYMERS

	Reactor Characteristics	Mixing Intensity	Remarks
<i>Step 1:</i> polymer dispersion	dosing into the feed pipe; turbulent conditions for 1 second are sufficient; no back mix	as high as possible (no floc destruction when mixing for one second)	very important, independent of sludge/polymer properties and polymer dose
<i>Step 2:</i> formation of discrete flocs	stirred, baffled reactor or static mixer; no back-mix; detention time 30 seconds	dependent on sludge properties and polymer dose; should therefore be variable	especially important when flocculation reaction is strong and polymer dose is high
<i>(Step 3):</i> formation of compact flocs (pellets)	rotating drum (according to Yusa, 1977); up to several minutes detention time	gentle mixing; homogeneous energy dissipation	only recommendable for stable flocs and high polymer doses (otherwise floc destruction!)

SUMMARY

A qualitative model has been presented that is suitable for the description of phenomena observed when flocculating highly concentrated sludges with organic polyelectrolytes. The results support the conception of an elastic floc network existing after initial mixing of polymer and sludge. A transition to discrete flocs proved to be favorable regarding the dewatering characteristics of the flocculated sludge.

Particle charge measurements in the filtrate revealed that at high polymer doses excess polymer stays in solution. This is not necessarily an indication of overdosing since with mixing time and/or increased mixing intensity this polymer can adsorb onto surfaces of floc fragments. By measurements of the mean floc size it could be demonstrated that the large and voluminous flocs formed after rapid-mixing are unfavorable for efficient dewatering. The highest content of sludge solids in the filter cake was obtained when rather small but compact flocs were formed. From the results it is concluded that optimum dewatering is achieved when a rather high polymer dose is applied, efficient rapid-mixing is provided and the flocculated sludge is passed through a mixing reactor with at least 1/2 minute detention time.

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REFERENCES

- Campbell, H.W. and Cresculo, P.J. (1982): The use of rheology for sludge characterization; *Wat. Sci. Tech.* **14** (6/7) 475-489
- Christensen, J.R.; Sørensen, P.B.; Christensen, G.L.; Hansen, J.A. (1993): Mechanisms for overdosing in sludge conditioning; *J. Environ. Eng. Div., ASCE*, Vol.119, No.1, pp. 159-171
- Firth, A.B.; Hunter, J.R. (1976): Flow properties of coagulated colloidal suspensions - III. The elastic floc model; *J. Colloid Interface Sci.*, Vol.57, Nr.2, pp.266-275
- Gregory, J. (1988): Polymer adsorption and flocculation in sheared suspensions; *Colloids and Surfaces*, Vol.31, pp.231-253
- Higashitani, K.; Kubota, T. (1987): Pelleting flocculation of colloidal latex particles; *Powder Technology*, Vol.51, pp.61-69
- Langer, S.L.; Klute, R. (1993): Rapid mixing in sludge conditioning with polymers; *Wat. Sci. Tech.*, Vol.28, No.2, 233-242
- Michaels, S.A.; Bolger, C.J. (1962): The plastic flow behavior of flocculated kaolin suspensions; *Ind. & Eng. Chem. Fundamentals*, Vol.1, Nr.3, pp.153-162
- Mühle, K., Domasch, K. (1991): Stability of particle aggregates in flocculation with polymers; *Chem. Eng. Process*, Vol.29, pp.1-8
- Novak, J.T.; Prendeville, J.F.; Sherrard, J.H. (1988): Mixing intensity and polymer performance in sludge dewatering; *J. Environ. Eng. Div., ASCE*, Vol.114, Nr.1, pp.190-198
- Otsubo, Y. and Umeya, K. (1984): Rheological properties of silica suspensions in polyacrylamide solutions; *Journal of Rheology*, Vol.28, No.2, pp.95-104
- Otsubo, Y. (1990): Elastic percolation in suspensions flocculated by polymer bridging, Vol.6, pp.114-118
- Sander, B. (1980): Flockenreifungszeit und mechanische Stabilität geflockter Klärschlämme. Meßmethoden und Bedeutung für die maschinelle Schlammwässerung; *Chemie-Ing.-Techn.*, Vol.52, No.3, synopsis pp.282-282, Microfiche 785/80
- Tadros, Th. F. (1985): Rheology of concentrated suspensions; *Chemistry and Industry*, Vol.7, pp.210-218
- Werle, C.P.; Novak, J.T.; Knocke, W.R.; Sherrard, J.H. (1984): Mixing intensity and polymer sludge conditioning; *J. Environ. Eng. Div., ASCE*, Vol.110, No.5, pp.919-934
- Yusa, M. (1977): Mechanisms of pelleting flocculation; *Int. J. of Miner. Process.*, Vol.4, pp.293-305