Settling behaviour of polymer flocculated water-treatment sludge I: analyses of settling curves

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Abstract

Settling behaviour of polymer conditioned water-treatment sludge was investigated in this study for the purpose of a better understanding of a so-called "CML30 method", which was developed in previous study to evaluate the optimum polymer dosage in sludge conditioning. The "CML30 method" is on the basis of a 30 min settling test in 100 ml measuring cylinders. In this study, the series of settling tests in 100, 500 and 1000 ml measuring cylinders were respectively performed and the settling curves (interfacial height to dose and time) were the main focuses for presentation and analyses in great detail in this paper. According to the experimental data presented in this study, settling behaviour may be controlled by both the growth of large sized floc and progressively decreased viscosity. The "speed-up" phenomenon in small polymer dose range obviously enhances the settlement and plays a critical role for the settling set in a 100 ml measuring cylinder at a special dose and at the settling time interval 5-30 min. It is such special observation that leads to the success of so-called *ad hoc* "CML30 method". However, sludge settling behaviour could be controlled by the formation of networked structure which is involved in excess polymer during the large

range (say over 10 mg/l for the case tested) of polymer doses. The higher liquid viscosity values derived from excess polymer will increase the drag force for the resistance of the settlement. In addition, wall effects are likely to interplay with the internal networked structure in large dosed region.

Keywords: Alum sludge; Flocculation; Polymer dosage; Settlement; Viscosity; Wall effect

1. Introduction

Over recent years, considerable attention has been focused upon the treatment and disposal of wastewater sludges. Relatively little attention has been given to water treatment sludge, which is commonly known as alum sludge since aluminium sulphate is the most widely used coagulant for flocculating the raw waters. Alum sludge has been recognized as difficult to dewater and is often conditioned with polymer prior to dewatering. In the research of investigating the wide range of interactions between polymer and an alum sludge (derived from the treatment of upland-low turbidity, coloured waters), a simple test method termed as the “CML30 method” for gauging an optimum polymer dosage has been developed [1]. The “CML30” test method is a simple method based on 30 min settlement of polymer conditioned alum sludge in a 100 ml measuring cylinder. With increasing polymer dose, it is observed that the height of the sludge – supernatant interface passes through minimum (as shown in Fig. 2). It was demonstrated that existed minimum interfacial height at a polymer dose under 30 min settlement coincided with the minimum in the modified SRF (specific resistance to filtration) trend [1,2,3]. Since the SRF has been served as criterion to evaluate the optimum dosage for decades, the minimum interfacial height of settlement (at 30 min) could be regarded as an

optimum and was shown to be well correlated with the sludge solids concentration [1]. Of interest, as pointed out by Bache and Zhao [1], the "CML30 test method" shows the good agreement with modified SRF only in 100 ml measuring cylinder. It does not work in larger scale cylinders, this being a questionable feature of this simple method. As such, the existence of a consistent behaviour in the 100 ml cylinder is a physicochemical quirk. For this reason, the particular settlement test is described as "*ad hoc*". Although the "CML30 method" is a purely empirical approach, it provides a simple method and may be considered as a practical approach for use in-situ.

In order to gain a better understanding of the mechanisms controlling the pattern of behaviour in "CML30 test method", this paper presents experimentally more tests on the basis of 100, 500 and 1000 ml measuring cylinders. The main focus is the explanation and analyses of the settling behaviour via the response of settling curves.

2. Materials and methods

The sludge was obtained from a waterworks sludge holding tank following primary clarification using aluminium sulphate as the coagulant. Table 1 showed the properties of the alum sludge used in this study.

Table 1 Properties of alum sludge used in this study

The sludge was conditioned with Magnafloc LT25 (*Allied Colloids UK Ltd., now CIBA Speciality Chemicals Ltd.*), which is an anionic organic polymer. The polymer was prepared

as a 0.01% stock solution using nanopure water and used after 24 h. The stock solution was made up every 48 h. Table 2 showed the basic characteristics of LT25.

Table 2 Properties of polymer Magnafloc LT 25 used in this study

The basis of the static settlement test procedure is shown schematically in Fig. 1. Initially, groups of sludge conditioning process were performed with polymer dosages in the range 2 – 30 mg/l to be added to 200 ml sludge samples. In each run, a number of 200 ml sludge samples were conditioned with fixed polymer dose. Following polymer addition the sludge was subjected to 30 s of rapid mixing followed by 1 min slow mixing to promote flocculation. Thereafter, polymer conditioned sludge were transferred to numbers of 100, 500 and 1000 ml measuring cylinders, respectively, and allowed to settle. Diameters of 100, 500 and 1000 ml measuring cylinders were respectively 30, 48 and 63 mm. When polymer dosed sludge samples were transferred to relevant cylinders, each cylinder was in turn shaken gently and upside down by hand, this taking 15 – 20 s intervals for 8 cylinders during the beginning of settling. The position of the sludge / supernatant interface was recorded as a function of settling time.

Settling tests were performed on the basis of “short term” and “long term” cases. For the case of “short term” tests, after 30 min settlement samples of supernatant were withdrawn for viscosity, turbidity and polymer adsorption measurements. To investigate the effect of settling time on settlement behaviour, long term settling tests (up to 143 hours settlement) were carried out until the equilibrium position of sludge / supernatant interface was reached.

The supernatant viscosity of the conditioned sludge was measured using an Oswald viscometer (*PSL Ltd, Wickford, UK*) which was held in a water bath to maintain a constant temperature of 20 ± 1 °C. Polymer adsorptions were calculated according to the difference in polymer concentrations between dosed and residual polymer (in the supernatant of conditioned sludge). Measurements of polymer residual were undertaken using high performance liquid chromatography (HPLC) based on size exclusion chromatography (SEC) as described in Keenan et al. [4].

Fig. 1 [here]

3. Results and discussion

3.1. Settling behaviour by visual observation

Fig. 2 & 3 provided respectively the photographic description of settling behaviour of polymer dosed sludge (with solid concentration of 4,595 mg/l) in 100 and 500 ml measuring cylinder sets. Details of the development of settling profiles (settlement process to dose and time) in 100, 500 and 1000 ml measuring cylinders can be seen in Fig. 4(a,b,c).

Fig. 2 [here]

Fig. 3 [here]

Fig. 4 [here]

Seen from Fig. 2 and Fig. 4(a), at high polymer dose (>15 mg/l) and early times there is very rapid settlement, leading to the formation of a coarsely structured matrix of deposited solids. The settlement properties of this solids column appear to be largely insensitive to dose. Through time this layer slowly reduces in height as water is gradually released due to

compressive settlement of the solids matrix. Evidence from tests conducted in larger measuring cylinders (see Fig. 3 and Fig. 4(b,c)) also points to the existence of bridging forces at the container walls. According to the sludge conditioning tests, the optimum dose of polymer for the sludge used in this study was 10.0 mg/l (data not shown), which was evaluated by modified SRF [3]. The settlement heights (at 30 min) shown in Fig. 2 to 4 were generally within ± 3% of the mean settlement in the underdose regime and within ± 7% in the overdose regime.

A lower dosages (say < 5 mg/l) and times < 3 h, the effect of increasing dose is to enhance the rate of settlement (regarded as a free settlement phase). It is not until much longer settling times (say 20 h, but dependent on dose) that one sees evidence of the compression settlement noted above. At intermediate doses and early times (say < 3h) it is the interaction between the free settlement and the formation of the "elevated" settled layer at high doses that promotes the existence of the minimum. For times in the interval 5 to 30 min the minimum occurs at about 10 mg/l. At longer settling times, the minimum occurs at lower values of dose. Similar phenomena are observed in 500 ml and 1000 ml measuring cylinders, but they do not behave in the same way as the 100ml cylinder.

3.2 Wall effects

Fig. 5 shows a plot of relative height (h_t/h_0, where h_t and h_0 refer to the settling height at time of t and 0) against settling time derived from the settling data in different sized settling cylinders. It provides evidence that there exists the difference of settling behaviour of varied cylinders between small dose (2.0 mg/l) and large dose (30.0 mg/l) and possibly indicates a wall effect. At low dose the settling behaviour is largely independent of the size of the

containers. At high dose it is seen that the 500 & 1000 ml containers behave similarly. In contrast the plots show that the settlement is impeded in the 100 ml cylinder.

Fig. 5 [here]

It is well known that the wall effect is the response of the settling velocity decreasing corresponding to the decrease of the diameter of the sedimentation vessel. As noted in Fig. 5 the different settling behaviour with varied containers shows possibly an association with the wall effect because polymer dosing can bring about the shift of particle size towards to the large direction [2]. The ratios (λ) between the settling cylinder tube diameter to the floc mean diameter d_{50} [5] for the conditions of this study are listed in Table 3. Although there is no standard value of λ, from literature Chen et al. [6] pointed out that λ should be in the range of 200 – 1000 in which the wall effect might be negligible. For such a case, Jaara [7] reported the range of λ in 50 – 100. From Table 3 it appears that wall effects were significant during the settling tests carried out in this study, especially in the overdose range.

Table 3 Values of λ in settling tests (sludge SS = 4,595 mg/l)

3.3 "Speed – up" phenomena during settling process

Fig. 6 shows a plot of settling height against time in a semi – log form. It is seen clearly that the settling behaviour of polymer dose at 10.0 mg/l (optimum dose) and below shows a complex pattern of accelerated settlement and long – term "slow" settlement. The first of these is probably caused by the effects of flocculation. The latter phase is probably compressive settlement.

Fig. 6 [here]

Data shown in Fig. 6 provides ample evidence that the settling rate during underdose range accelerates. This “self-speed up” phenomenon was also reported by Chen et al. [6] who pointed out that the activated sludge zone settling curve (interfacial height vs. settling time) exhibited a “speed-up” period. Sometimes even more than one “speed-up” period existed. This made the settling behaviour a more complicated and caused reasonably by the “channelling phenomena” which happened sometimes. “Channelling” in zone settling process is defined as the creation of flow paths in a thickening suspension on a scale much larger than the size of the solid particles themselves [8]. Some sludges under certain conditions, if “channelling” happened, will release liquid in streams which are large and few in number when compared to the flow paths developed during uniform seepage. The “channelling” enhances settling velocity, which is very preferable in settling operations. Nevertheless, it brings about the difficulty to describe the settling behaviour. Ramalho [9] reported that in settlement of flocculated suspension the settling velocity would increase with the growth of the flocculated clusters. Therefore, the “speed-up” phase of this study may be attributed to the flocculation during settlement. As noted in Fig. 6 this “speed-up” phenomenon only occurred in underdose range and was considered reasonably the controlling factor of settling behaviour. Particularly, it is noted from Fig. 6 that the “speed-up” phenomenon was firstly occurred for polymer dose of 10 mg/l set at settling time around 5-30 min, then the set of polymer dose of 5 mg/l at the time of 6-80 min. For the case of polymer dose of 2 mg/l set, the “speed-up” phase started from 1 hour and lasted until 10 hours of settling. It is the fact of “first happened speed-up” of polymer dose of 10 mg/l set in 100 ml cylinder that controls the “CML30 method” and makes this simple method coincide with modified SRF for the optimising polymer dose during alum sludge conditioning.

3.4 Viscosity of supernatant and its effect on settling behaviour

Previous results have demonstrated that the viscosity of the supernatant of a polymer-dosed sludge changed with the polymer dosage [1]. In this phase of tests, supernatant of polymer-dosed sludge samples was withdrawn immediately after 30 min settlement and its viscosity was measured by using an Ostwald Calibrated Viscometer at 20 ± 1°C. The plot shown in Fig. 7 illustrates the pattern of viscosity from decrease to increase with the increase of polymer dose.

Fig. 7 [here]

Investigations carried out by Dental & Abu - Orf [10], Dental et al. [11] and Papavasilopoulos [12] suggested that decreases in viscosity could be attributed to decreases in the concentration of fine particles in the supernatant. Increases in viscosity were attributed to excess polymer in the bulk. Fig. 7 also displays the corresponding of turbidity measurements of the supernatant (for SS = 4,595 mg/l set). The feature of sharp falling turbidity (dose < 2 mg/l) and then essentially constant (dose > 5.0 mg/l) is evident in Fig. 7. A comparison of the trends shown in Fig. 7 suggests that when the dose exceeds 5.0 mg/l, changes in turbidity are unlikely to affect the viscosity — indicating that the changes of viscosity may be derived from other factors such as the dissolved substances. According to the viscosity model developed by Bache and Papavasilopoulos [13], increases in viscosity in the overdose range may be attributed to the excess polymer or the saturation adsorption of polymer. This can be confirmed by Fig.8 in this study. Fig. 8 illustrates the results corresponding to the cases of settlement in the 100, 500 and 1000 ml cylinders with sludge solids concentration of 4,595 mg/l. It provides evidence that residual polymer increases rapidly in the overdosing range. A

more viscous supernatant will lead to increased resistance to water release as pointed out by Johnson et al. [14].

Fig. 8 [here]

The direct effect of viscosity on settling behaviour is shown in Fig. 9 where two parallel settling tests (aimed to provide the comparative data) were undertaken (using 100 ml measuring cylinder) for the sludge samples with solids concentration of 4,595 mg/l at the polymer dose of 20.0 mg/l (overdose). In one test supernatant was carefully withdrawn and replaced by nanopure water (μ = 1.0008 mm^2/s). Data in Fig. 9 shows clearly that the replacement of polymer dosed sludge supernatant (μ = 1.0683 mm^2/s for the case of polymer dose of 20.0 mg/l) can enhance the settling behaviour, indicating that the viscosity derived from excess polymer has a significant effect on the settling behaviour.

Fig. 9 [here]

Overall, the falling and constant turbidity in underdose range leads to the decrease of viscosity and excess polymer in the overdose region results in the increase of viscosity. Hence the viscosity may be one of the principal factors influencing the settlement behaviour.

4. Summary and conclusions

The aim of this investigation was to gain insight into the controls on the "CML30 method" such as illustrated in Fig. 2. Since the "CML30 method" depended fully on the settling behaviour of polymer flocculated waterworks sludge (in author's study) and appears to be specific to the settlement in a 100 ml measuring cylinder in the time interval 5-30 min, the series of settling tests in 100, 500 and 1000 ml measuring cylinders were performed and the

settling curves (interfacial height to dose and time) were the focuses for presentation and analyses in this paper.

In the small polymer doses (under 10 mg/l for the case of sludge solid concentration of 4.4 g/l to 4.6 g/l in this study), settling behaviour may be controlled by both the growth of large sized floc and progressively decreased viscosity. The "speed-up" phenomenon in these range obviously enhances the settlement and plays a critical role for the settling set in a 100 ml measuring cylinder of special polymer dose at 10 mg/l. It was evidence that this special set has the "speed-up" phase occurred at the time interval 5-30 min. Such special observation leads to the success of so-called *ad hoc* "CML30 method" for gauging the optimum polymer dose. However, during the large range (say over 10 mg/l for the case tested) of polymer doses sludge settling behaviour could be controlled by the formation of networked structure which is involved in excess polymer. The higher liquid viscosity values derived from excess polymer will increase the drag force for the resistance of the settlement. In addition, wall effects are likely to interplay with the internal networked structure in large dosed region, this being most pronounced in the 100 ml cylinder.

It is necessary to state that there are many unresolved difficulties and problems in trying to integrate the phenomena which control the settlement behaviour. It is believed that the settling behaviour of flocculated suspension is complex, depending on factors such as floc size, density, velocity, viscosity, flocculation and wall effect as well as the formation of aggregate structures. However, many of such are beyond this paper and remain the further investigation.

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Table 1. Properties of alum sludge used in this study *

Suspend solid (mg/l)	pH	SRF ($\times 10^{12}$m/kg)	CST (s)	Viscosity (mm^2/s) (filtrate)
4,400~4,600	6.6~6.9	58.6~82.7	57.3~68.9	1.0045~1.0122

* SRF: Specific Resistance to Filtration; CST: Capillary Suction Time.

Table 2. Properties of polymer Mgnafloc LT 25 used in this study

Type	Molecular weight	Charge (% by weight)	Concentration (%)	Manufacturer
Anionic	$(10\sim15)\times10^6$	15~30	0.01	CIBA Speciality Chemicals Ltd, UK

Table 3 Values of λ in settling tests (sludge SS = 4,595 mg/l)*

Polymer dose (mg/l)	Mean floc diameter d_{50} (mm)	Values of λ		
		100 ml cylinder	500 ml cylinder	1000 ml cylinder
0	0.197	152.3	244.7	319.8
2	0.766	39.2	62.9	82.2
5	1.012	29.6	47.6	62.3
10	1.652	18.2	29.2	38.1
15	1.800	16.7	26.8	35.0
20	1.829	16.4	26.4	34.4

* Diameters of 100, 500 and 1000 ml measuring cylinders were respectively 30, 48 and 63 mm.

Figure Captions

Fig. 1 Schematic methodology of static zone settlement test

Fig. 2 Photographic response of interfacial height to dose for a sludge of 4,595 mg/l solids concentration in 100 ml measuring cylinders at the settling time of 15 s (above) and 30 min [1] (bottom), respectively. (Numbers on the cylinder represent the polymer dose in mg/l.)

Fig. 3 Photographic response of interfacial height to dose for a sludge of 4,595 mg/l solids concentration in 500 ml measuring cylinders at the settling time of 15 s (above) and 30 min (bottom), respectively. (Numbers on the cylinder represent the polymer dose in mg/l.)

Fig. 4 Responses of interfacial height to time and dose for a sludge with solids concentration of 4,440 mg/l in measuring cylinders of: (a) 100ml[1], (b) 500ml and (c) 1000ml [1]

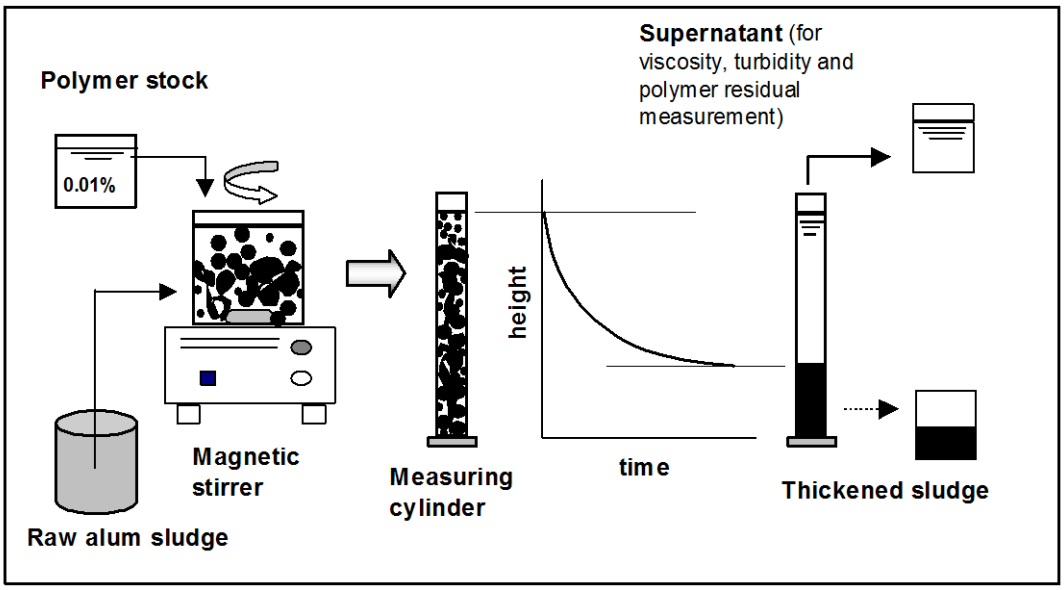
Fig. 5 Relative settling height as a function of time for varied cylinders atsmall and large polymer dose (SS = 4,595 mg/l)

Fig. 6 Showing "speed-up" behaviour during settling process (using 100 ml measuring cylinder, SS = 4,595 mg/l)

Fig. 7 Pattern of supernatant viscosity and turbidity with the polymer dosage (SS=4,595 mg/l) (Samples were withdrawn at 30 min settling.)

Fig. 8 Profile of polymer residual in polymer dosed sludge supernatant (SS=4,595 mg/l)

Fig. 9 Effect of supernatant viscosity to the settling behaviour (predosed at 20.0 mg/l with polymer, using 100 ml measuring cylinder, SS = 4,595 mg/l)



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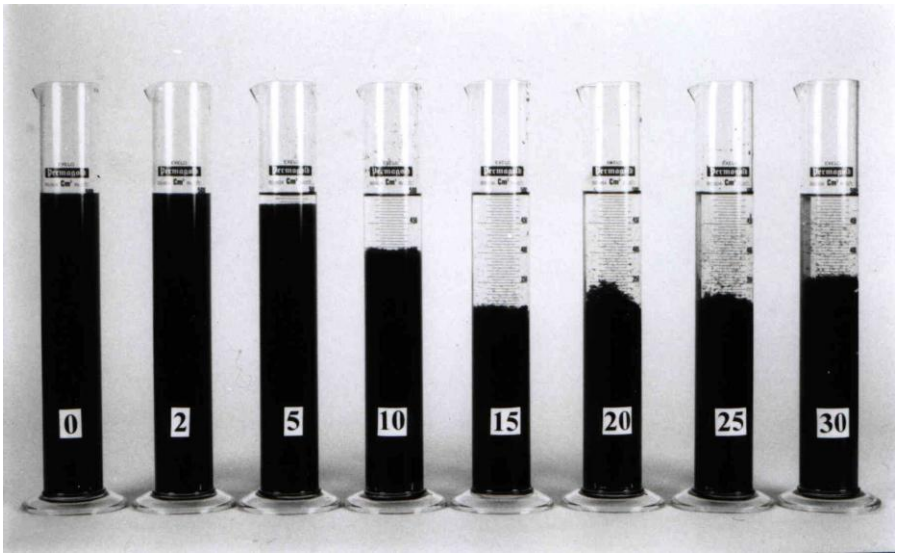

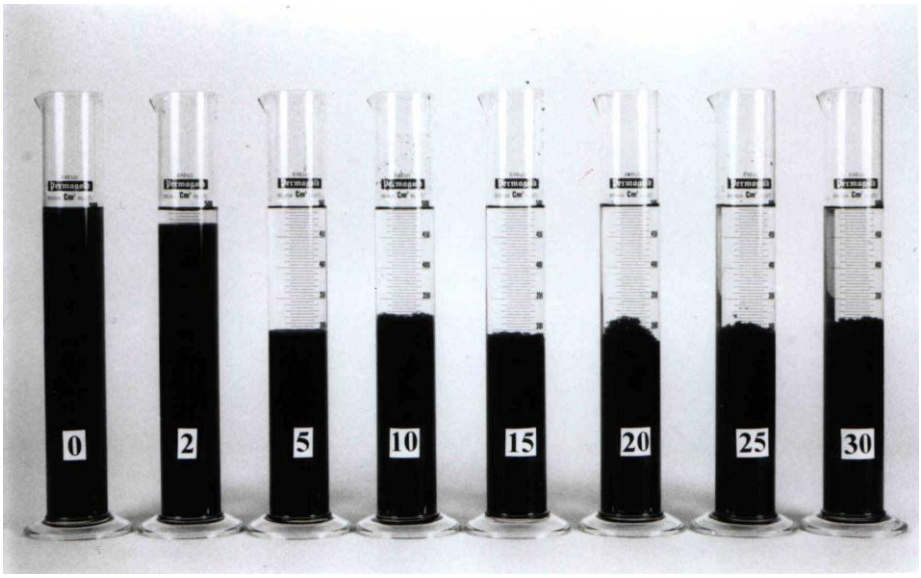

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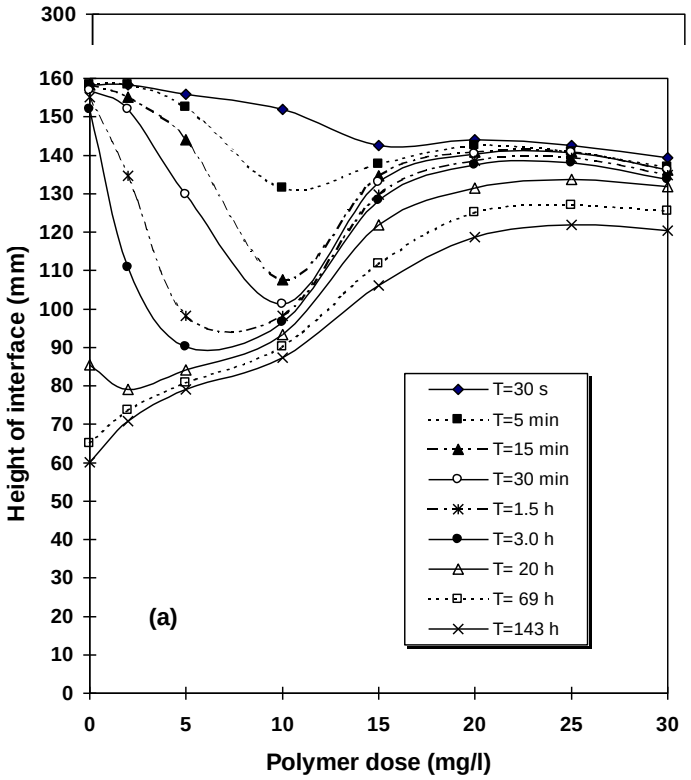

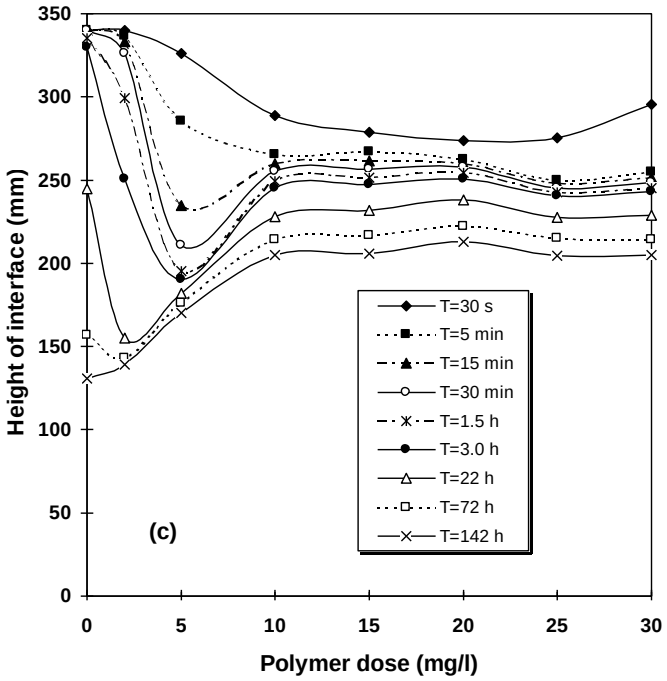

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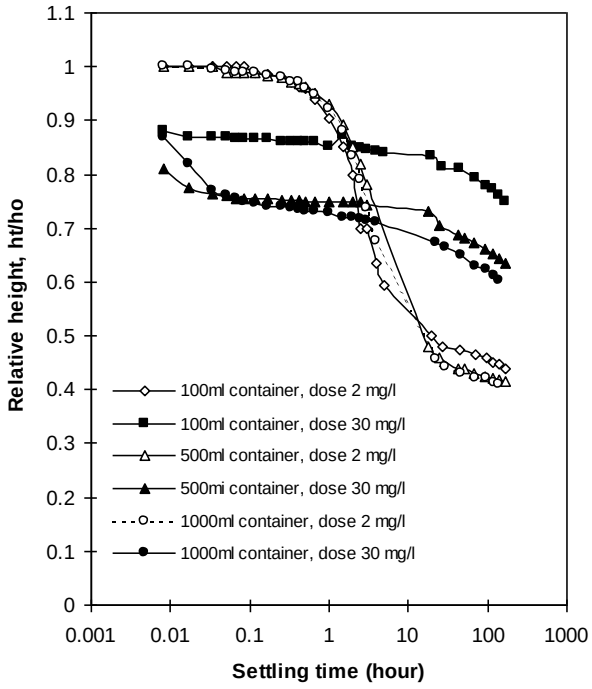
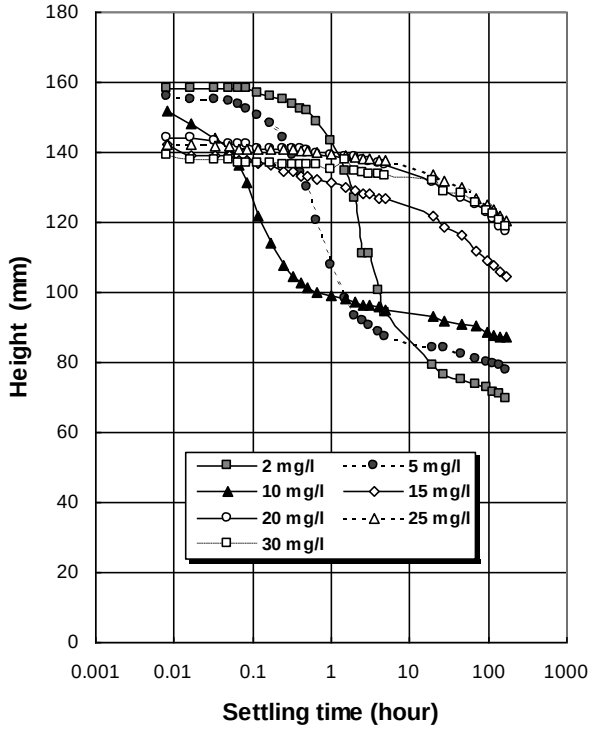


Fig. 5 Relative settling height as a function of time for varied cylinders at small and large polymer dose (SS = 4,595 mg/l)



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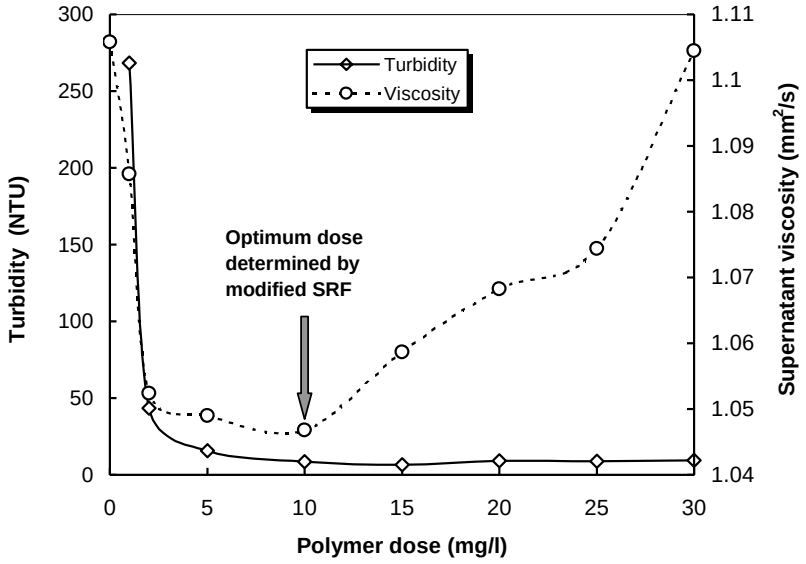
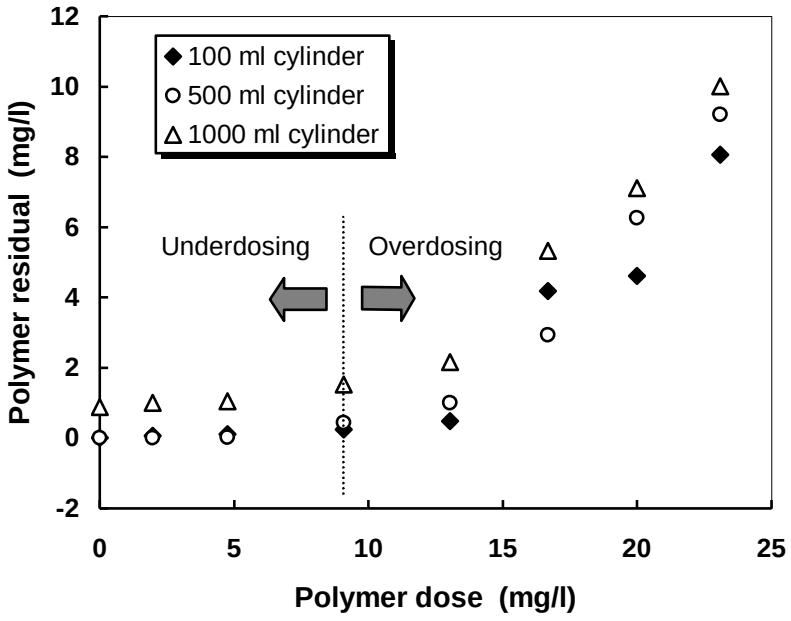


Fig. 7 Pattern of supernatant viscosity and turbidity with the polymer dosage (SS=4,595 mg/l) (Samples were withdrawn at 30 min settling.)



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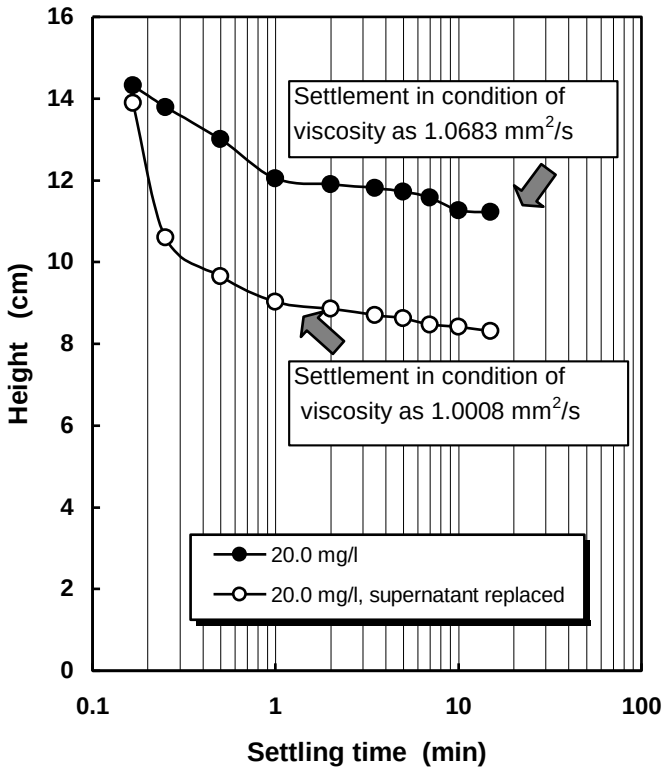

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