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Effects of polymer conditioning on alum sludge characteristics: a review

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Abstract

This paper is concerned principally with summarizing recent information on the effects of polymer conditioning on alum sludge characteristics. Alum sludge refers to the by-product created during the treatment of raw waters using aluminium sulphate as the coagulant. In spite of the limited published data, evidence has shown that polymer dosing can lead to a shift towards: large size aggregates; higher density and more compact flocs; more compressible sludge and an obvious change of sludge rheology properties as well as the bound water content. Certain discrepancies in the effects of polymer on alum sludge characteristics indicate the complexity not only in the physico-chemical process which leads to formation of flocs but also in the characterization of sludge/sludge flocs. Preliminary research work aimed to reveal the role of hydroxide precipitate (derived from aluminium sulphate) during alum sludge conditioning and dewatering and the interaction with polymer highlights the forthcoming research focus.

1 Introduction

Polymer conditioning has long been employed to pre-treat sludge in order to enhance its dewaterability. Over recent years, a lot of attention has been focused upon the treatment and disposal of wastewater sludges. Relatively little attention has been paid 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. It is noted that, for alum sludge derived from upland coloured waters, 45 –50 % of the dry mass arises from the coagulant [1] and it is therefore expected to have a major bearing on the overall sludge characteristics. In recent investigations of the alumino-humic, Bache *et al.*[2] suggested that the hydroxide precipitate appeared to be the prime determinant of the overall floc properties and the sludge dewatering characteristics. This is supported by the study of Papavasilopoulos and Bache [3] whereby it was shown that the hydroxide precipitate interaction with a nonionic polymer was critical in terms of establishing optimum conditioning and dewatering.

It is believed that the change of sludge dewaterability is derived from changes in sludge characteristics after polymer conditioning. Because sludge is a particularly difficult material to characterize in a quantitative manner, a description of the effects of polymer conditioning on sludge properties is also difficult. The aim of this paper is to provide an updated overview of the alterations in principal alum sludge characteristics after polymer addition, albeit based on limited data available in current literature. As a necessary preamble, the fundamental aspects for describing alum sludge characteristics are also discussed.

2 Characteristics of alum sludge

The characteristics of alum sludge can be described in different categories, such as physical and chemical aspects etc. Since sludges are considered as flocs (solid phase) and bulk water (liquid phase), their characteristics are mainly controlled by floc properties.

Floc size, density and fractal dimension characterize the sludge's physical properties. An accurate measurement of floc size is difficult because of the physicochemical nature of flocs. The methodologies for such sensitive measurements are prone to errors and can often be misleading. Three principal methods have been reported for floc size / size distribution measurement [4]. Floc size and density are related in the form of:

$$\rho_e = A\, d^{-n} \qquad (1)$$

where d is a representative diameter and ρ_e is the effective density of the floc. A and n are fitting constants. For humic flocs, ρ_e is sensitive to the alum dose and pH and was found to be of the order of 5.5 kg/m^3 [1]. There are several experimental techniques available for the measurement of floc density including sedimentation techniques, light scattering and other methods. A brief review of some of these techniques is provided by Gregory [5]. Fractal dimension, D_F, is a quantitative measurement of floc structure and provides an indication of how the particles are organized with the floc interior: the higher the fractal dimension (maximum 3; n in Eq.(1) is related to D_F by $D_F = 3 - n$), the more compact the floc. Bache and Hossain [1] found that humic flocs could be characterized by D_F = 1.0. Wu *et al.* [6] found D_F for raw alum sludge to be 1.18.

The moisture content of a sludge is a critical variable because of its influence on the sludge volume. The water is not 'free' in thermodynamic terms in that it is 'bound' or tied chemically or physically into the floc structure. Up to the present, there is neither a universal definition of bound water, nor a standard method for its measurement. For this reason, care should be taken in the interpretation of the data concerning bound water in literature because of the variety of definitions and means of measurement. In literature, descriptions are given of various techniques used to examine the bound water content of sludges. Lee [7] and Johnson [8] gave a brief summary. Some of the methods are as follows: Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), vapour pressure depression, Nuclear Magnetic Resonance (NMR), drying tests, expression and centrifugal settling. Some of the techniques used are not independent, but are related since the underlying principles are the same.

Sludges are known to be compressible in the sense that the floc structure deforms in response to the applied pressure. Sludge compressibility, S, is defined in terms of the specific resistance to filtration (SRF) in the form:

$$\frac{SRF_i}{SRF_0} = \left(\frac{P_{t,i}}{P_{t,0}}\right)^s \qquad (2)$$

Terms $P_{t,i}$, $P_{t,0}$ refer to the applied pressure and a reference pressure respectively. SRF_i and SRF_0 are the corresponding values of the specific resistance. Parameter S can be obtained from a log-log plot of SRF_i/SRF_0 against the relative applied pressure ratio. Values of S such as 1.03 [9] and 1.0 [10] have been determined for alum sludges.

Rheology can be defined as the study of the properties and behaviour of matter in the fluid state. It describes the deformation of a body under the influence of stresses. The characteristic rheological properties of a sludge made of flocs can be summarised as shear thinning, plasticity, yield value and thixotropy behaviours [11]. Glasgow and Kim [12] quoted the following form to express the shear stress (τ) and to explain how the energy changes when increasing shear breaks down extensive aggregate networks:

$$\tau = \tau_N + \tau_{CR} + \tau_V \qquad (3)$$

τ_N depends on aggregate size volume fraction and bind force, and the orientation of aggregates in the network. τ_{CR} represents the stress required to break network bonds and separate the constituent flocs. τ_V is the stress required to overcome viscous drag forces arising from relative motion between the structure and the suspending medium.

3 Effects of polymer addition on alum sludge characteristics

3.1 Effect on floc size

A number of investigators reported their experimental results about floc size during polymer conditioning. Among these, there exist two response trends of mean floc size with an increase of polymer addition. One is a monotonic increase, and the other is the attainment of low increase rate or a plateau.

Wu *et al.* [6] reported that the average diameter of polymer conditioned alum sludge floc, measured by image analysis, significantly increased with polymer dose, as shown in Fig. 1. In their recent paper, Chu and Lee [13] noted a marked increase in floc size in polymer flocculation of clay and activated sludge. Their data are quoted in Table 1.

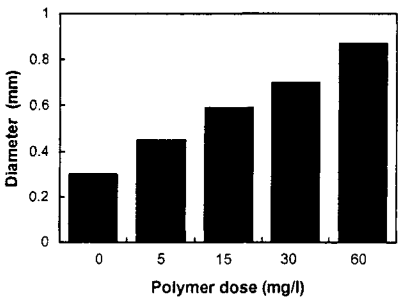

Figure 1: Effects of polymer dose on the average floc diameter of alum sludge measured by image analysis (after Wu *et al.* [6])

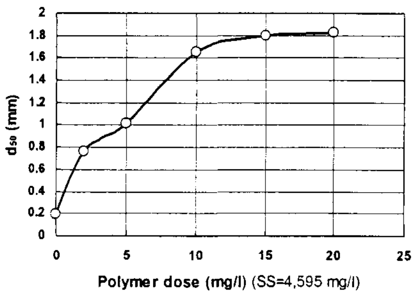

Figure 2: Median diameter (d_{50}) versus polymer dosage for an alum sludge conditioned with polymer *Magnafloc LT25* (after Zhao [16])

Table 1: Mean particle diameter on polymer flocculation (after Chu &Lee[13])

Polymer dose (ppm)	Clay sludge mean diameter (μm)	Activated sludge mean diameter (μm)
0	5.06	60.1
20	19.2	129
40	-	206
100	59.4	-
120	-	358
220	150	-

Also with clay sludge, Wen *et al.* [14] provided evidence of a definite increase in mean floc size with increasing polymer dose. However, at a still high polymer dose, the floc size grew at a slower rate. More evidence is presented in a paper by Langer *et al.*[15], in which the mean floc size at different polymer doses was plotted as function of mixing speed. The closing of trend lines with increasing dose indicates a marked reduction in the sensitivity of the floc size to dose. Zhao [16] investigated the interaction between a polymer and an alum sludge and measured particle size distributions using an image analysis technique. It is noted that the shift in size to larger flocs reaches a plateau as illustrated in Fig. 2. From the reported studies it is evident that the polymer dosing leads to a shift in the particle size towards groupings of larger diameter, a facet which aids water release.

3.2 Effect on floc density and fractal dimension (D_F)

Knocke *et al.* [17] used isopycnic centrifugation technology to measure the floc density of sludge. The results indicated that water released via polymer addition caused an increase in floc density. With regard to flocs derived from treatment of coloured waters, Dulin and Knocke [18] showed that there was a decrease in sludge floc density with the presence of organic matter in the floc matrix. Their study showed that the incorporation of organic matter into the floc phase yielded a floc structure of slightly decreased size and greater water content. Wen *et al.* [14] provided evidence that the floc density and fractal dimension of synthetic sludge were insensitive to the polymer doses. However, general inspection of the data suggests that there is some evidence of higher densities being associated with higher doses, but this would need to be demonstrated statistically. More recently, in Zhao's [16] study, it was evident that the effective density of alum sludge flocs increased with increasing polymer dosages for the range examined. Originally, floc size and effective density data were derived from the image analysis system after the sedimentation of individual flocs. The trend lines in each polymer dose were calculated using a least squares analysis and are summarized in Fig. 3.

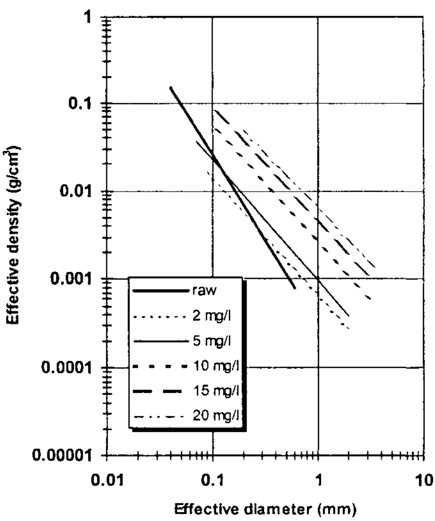

Figure 3: Trend lines of floc size and effective density with polymer dosage for an alum sludge conditioned with polymer Magnafloc LT25 (after Zhao [16])

For an alum sludge (solids concentration of 3.82 %, dry density of 2,278 kg/m^3), Wu *et al.* [6] reported D_F increased with polymer doses (from 5.0 – 60.0 mg/l) in the range 1.04 to 1.83, indicating that the degree of sludge floc compactness increases with polymer dose. Wu *et al.* [6] explained that, at high polymer dose, each floc is covered with several polymer molecules and, after many interparticle collisions, large granular flocs are produced as each particle is bound to several others. At low polymer dose, it seems that the polymer does not greatly influence the 'necklace structure' for humic flocs.

3.3 Effect on sludge compressibility

It appears that polymer conditioning could render the sludge more compressible. Novak and O'Brien [19] reported that alum sludge compressibility increases greatly with the addition of polymers. In most instances, the maximum value of S was found to occur at or beyond the optimal polymer dose. Sorensen *et al.* [20] demonstrated that the extreme compressibility of sludge cake resulted in a filtrate flow which is independent of the applied pressure.

3.4 Effect on water binding

Research on the effects of polymer conditioning on the bound water content of sludge reveals certain discrepancies. Katsiris and Kouzeli - Katsiri [21] reported decreasing bound water content with increasing polymer dose (decreased by up to 50 % for a dose corresponding to a minimum SRF). In agreement with this, Robinson and Knocke [22] also showed that improved dewatering rates of waste chemical and biological sludges coincided with a decrease of 50 % in the bound water content. Finally, Knocke *et al.* [17] showed that polymer conditioning of both alum sludge and lime sludge caused a release of floc water at a percentage which was typically in the range of 25 – 40%. These investigators agreed that the decrease in bound water is attributed to the replacement of water molecules on the solid surface by the polymer molecules. In contrast, Smollen [23] reported an increase in bound water content with polymer addition. She suggested that the excess polymer molecules attached to the particle surface could absorb moisture from the bulk water phase, which contributes to the observed increase in bound water. Wu *et al.* [6] investigated the effects of polymer dose on bound water content of an alum sludge. Interestingly, they found that the bound water of alum sludge first decreases and, after passing some minimum point, increases with further polymer dose. Wu *et al.* [24] suggested that interparticle squeezing (the replacement of physically / chemically absorbed surface water molecules by absorbed polymer molecules) is the more probable cause of the decrease in the bound water because the interparticle squeezing should force out mainly the interstitial water. At high polymer dose, the water molecules adsorption onto polymer molecules should be responsible for the increase in bound water.

3.5 Effects on sludge liquid phase viscosity

Studies by Christensen *et al.* [25] and Abu-Orf & Dentel [26], dwelled on the viscosity of the liquid phase of a sludge. From measurements on the filtrate of an anaerobically digested sewage sludge, Christensen *et al.* [25] observed that the viscosity of the filtrate increased with increasing polymer dosages, a feature which was attributed to the presence of excess polymer in the liquid phase (Fig. 4). According to Christensen *et al.* [25] the increased viscosity of the liquid phase, rather than reduced flocculation performance, was a clear sign of polymer overdosing. In the case of Abu-Orf and Dentel [26], they measured the viscosity of anaerobically digested sewage sludge centrate and observed that the viscosity of centrate passed through a minimum (Fig. 5).

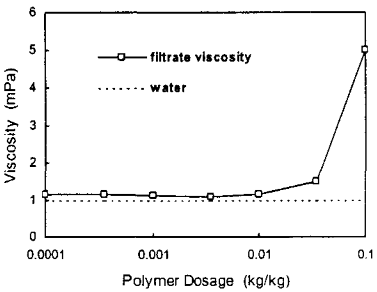

Fig. 4 Filtrate viscosity of anaerobically digested sewage sludge as a function of a cationic polymer dosage (after Christensen *et al.*[25]).

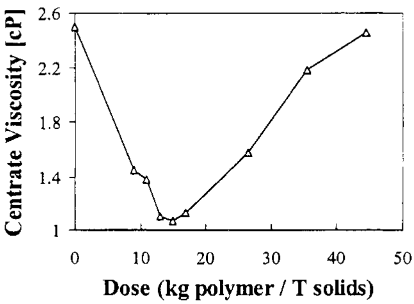

Fig. 5 Centrate viscosity vs. polymer dose. Polymer was cationic copolymer of acrylamide (after Abu-Orf & Dentel [26]).

The general behaviour of the viscosity trend with respect to the polymer dose is explained by Abu-Orf and Dentel [26] on the basis that viscosity of a suspension is influenced either due to increased solids concentration or due to the build-up of unadsorbed viscous polymer. In the underdosed region, small particles can easily escape the sludge flocs and remain in the supernatant since there is not enough polymer to destabilise the particles' surfaces, thus giving rise to a higher viscosity. As the dose increases, the centrate becomes clearer, fine particles aggregate into larger flocs and the viscosity reaches a minimum, acquiring a value close to that of water. It appears that, from that dose onwards, the viscosity is mainly controlled by the presence of excess unadsorbed polymer molecules, a view confirmed by Papavasilopoulos [27], Papavasilopoulos and Bache [3] and Zhao [16] in alum sludge conditioning with polymer.

4 Discussion

It is widely accepted that the polymer conditioning of alum sludge can aggregate the small particles to form flocs and result in a shift towards a larger size of floc with an increase in polymer doses. This shift has been proven to be the major effect in improving the sludge dewaterability. However, particle size distribution does not always show a unique effect on sludge dewaterability, e.g. Wen *et al.* [14] found that the floc size had no correlation with the optimal polymer dose determined on the basis of sludge dewaterability. In addition, polymer conditioning can produce denser and more compact flocs, but there is evidence to show that the optimal dewatering behaviour does not occur in flocs with the highest density and most compact structure [16]. Although polymer addition has different effects on the bound water content, the changes of bound water content do not appear to be a major determinant of the final degree of sludge cake dryness [17]. It is noted that the polymer addition can make the sludge more compressive. This could have negative effect on sludge dewaterability by causing cake void closure which can impede continued dewatering [28]. If the polymer is overdosed, the excess polymer can increase the sludge viscosity. This has been shown to cause filter medium clogging by the interaction of excess polymer with fine particles in sludge bulk solution. It can result in misjudgement of the optimum dose [29].

Overall, the most important benefit of polymer conditioning of alum sludge is the improvement in sludge dewaterability. This benefit is based on the proper use of polymers and their integrated effects on sludge characteristics. Here, the term 'proper use' includes 'single use', 'dual use' and even the use of polymer with other materials, i.e. 'combined use' [28, 30].

It should be noted that, according to the preliminary investigation carried out by Papavasilopoulos and Bache [3], the hydroxide precipitate within alum sludge appeared to be the prime determinant of the overall floc properties and was critical in terms of establishing optimum conditioning and dewatering. Therefore, the role of hydroxide precipitate in alum sludge and the interaction with polymers during conditioning and dewatering should be given more attention.

5 Conclusions

The results available to date on the effects of polymer conditioning on alum sludge characteristics indicate that polymer dosing can result in a shift towards larger size aggregates of flocs although the floc size may reach a plateau with the increase in polymer doses. Further evidence demonstrates higher densities being associated with higher polymer doses. This leads to a reasonable belief that the degree of sludge floc compactness increases with polymer dose, i.e. a increased value of fractal dimension (D_F). Research on bound water content shows certain discrepancies, but there is evidence to suggest that the minor effect of bound water content on dewatered alum sludge moisture content. Polymer conditioning has been found to influence sludge rheology properties, particularly the sludge liquid phase viscosity.

Current knowledge to reveal the nature of polymer conditioning of alum sludge is still somewhat superficial due to the inherent complexity of the conditioning process and the difficulties of quantitative description of sludge characteristics. As up to 50 % of the dry mass of dewatered alum sludge can arise from the aluminium sulphate, more research work to reveal the role and the interaction between polymer and aluminium sulphate is highly desirable.

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