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<td><strong>Authors(s)</strong></td>
<td>Ma, W.; Zhao, Y.Q.; Kearney, P.</td>
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<tr>
<td><strong>Publication date</strong></td>
<td>2007-01</td>
</tr>
<tr>
<td><strong>Publication information</strong></td>
<td>Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances &amp; Environmental Engineering, 42 (7): 961-968</td>
</tr>
<tr>
<td><strong>Publisher</strong></td>
<td>Taylor &amp; Francis</td>
</tr>
<tr>
<td><strong>Link to online version</strong></td>
<td><a href="http://dx.doi.org/10.1080/10934520701370261">http://dx.doi.org/10.1080/10934520701370261</a></td>
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<td><a href="http://hdl.handle.net/10197/3171">http://hdl.handle.net/10197/3171</a></td>
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<tr>
<td><strong>Publisher's statement</strong></td>
<td>This is an electronic version of an article published in Journal of Environmental Science and Health, Part A 42(7): 961-968 available online at: <a href="http://www.tandfonline.com/doi/abs/10.1080/10934520701370261">http://www.tandfonline.com/doi/abs/10.1080/10934520701370261</a></td>
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<td>10.1080/10934520701370261</td>
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A Study of Dual Polymer Conditioning of Aluminium-based Drinking Water Treatment Residual

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ABSTRACT

Conditioning of an alum-based water treatment sludge by single and dual polymers was investigated in this study. Capillary suction time (CST), specific resistance to filtration (SRF) and settling rate of conditioned sludge were used to evaluate the sludge dewatering characteristics. Sludge dewaterability resulting from single and dual polymer conditioning were compared for the purpose of exploring the validity and effectiveness of dual polymer conditioning strategy. Unlike activated sludge derived from wastewater treatment, results from this study have demonstrated that conditioning of the alum sludge by the combined use of an cationic polymer (FO-4140) followed by

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an anionic polymer (LT-25) does not exhibit considerable advantage in further improvement of sludge dewaterability with comparison of single polymer conditioning. This study supports the view that for alum-based water treatment sludge, inter particle bridging seems to be the dominative mechanism and the charge neutralization plays a less important role in the conditioning process. In addition, an intrinsic relationship between CST and SRF was deducted and tested via the experimental data obtained from the study.

Key Words: Alum sludge; Capillary suction time (CST); Conditioning, Dewaterability; Polymer; Specific resistance to filtration (SRF).

INTRODUCTION

Alum is used in the coagulation of raw waters in most of the water treatment works worldwide. The waste generated is thus termed as alum sludge when aluminium sulphate is employed as the primary coagulant. In Ireland, alum sludge is chemically conditioned and mechanically dewatered before its final disposal as a waste for landfill. Polymers are the primary choice as chemical conditioners for alum sludge conditioning and various organic polymers are currently used, such as anionic polymer Magnafloc LT-25 and cationic polymer FO-4140 PWG etc. With regard to the role of polymer in
conditioning, two dominating mechanisms are involved: charge neutralization and inter
particle bridging. \cite{1,2}

In order to obtain good dewaterability, research has now prompted a change to the dual
polymer conditioning processes owing to their advantages of higher mass content in
dewatering and more efficient sludge/liquid separation. For example, Lee and Liu \cite{3}
proposed that when activated sludge was pre-conditioned with cationic polymer, it
adsorbed on the biosolids particles and primary flocs were formed. The ensuing addition
of non-ionic polymer with the same amount of cationic polymer then became adsorbed
on the loops and tails of the cationic polymer by hydrogen bonding and Van der Waals
force. Consequently, the adsorption of mixed polymer on the particle surfaces formed
an extended polymer conformation. The thicker and more expanded adsorption layer
contributed to the enhanced flocculation and enhanced dewaterability. Wang et al. \cite{2}
studied the dual conditioning of activated sludge utilizing polyampholyte T204 in
combination with either ferric chloride or polydiallyldimethyl ammonium chloride
(PDADMAC). Their results showed that although T204 was not an effective conditioner
when used alone, the combined use of PDADMAC followed by T204 could result in
better dewaterability. They explained that the dual conditioning strategy could enhance
flocculation of sludge particles and resulted in large and strong flocs, thus improving
sludge dewaterability. However, it has been evidenced that such the beneficial dual
conditioning strategy seemed not the case for water treatment sludge conditioning, as
reported by Ayol et al. \cite{4} By investigating the dual polymer conditioning of a ferric
chloride-generated water treatment sludge using Percol LT22S (a high molecular weight cationic acrylamide-based copolymer) and Percol LT20 (a high molecular weight non-ionic polyacrylamide homopolymer), Ayol et al. [4] have demonstrated that the conditioning using cationic polymer combined with the nonionic polymer was not significant for improving the dewaterability of water treatment works sludge. In contrast, the drawback was the installation, operation and control process in dual conditioning strategy. Thus, they concluded that the dual polymer conditioning of water treatment sludge cannot be recommended.

Keeping in mind of the above, it is noted that the dual polymer conditioning exhibited different effects on the dewaterability of biosolids (sewage sludge) and water treatment sludge (residual), respectively. However, information from the dual polymer conditioning of water treatment residual is extremely lack in the literature. For this reason, this study focused on the investigation of dual polymer conditioning of an aluminium-based drinking water treatment residual. Both a cationic polymer FO-4140 PWG and an anionic polymer Magnafloc LT-25 were utilized in alum sludge dual conditioning. Capillary suction time (CST) and specific resistance to filtration (SRF) together with settling rate of conditioned sludge were used as indexes to evaluate the sludge dewaterability. Sludge dewatering characteristics resulting from single and dual polymers conditioning were compared. The purpose of this study was to investigate whether enhanced dewaterability of alum sludge could be achieved through the combined use of cationic and anionic polymer as dual conditioners, and to elucidate
preliminarily the mechanisms in dual polyelectrolyte conditioning system. In addition, correlations between CST and SRF are deduced theoretically and tested according to the current experimental data although some empirical relationships of CST and SRF have been reported from the literature.

**MATERIALS AND METHODS**

The alum sludge used in this study was collected from the sludge holding tank of the Ballymore Eustace Water Treatment Works (in Southwest Dublin) where aluminium sulphate is used as the primary coagulant (at a dose of 42-60mg/L) for treating raw water extracted from a nearby reservoir. The properties of this alum sludge are listed in Table 1. The total solid (TS), suspended solid (SS) and dissolved solids (DS) of the sludge were determined using standard methods.\(^{(5)}\) The value of pH was measured by pH Meter (WTW pH 325) immersing the electrode 2 cm below the sludge/air interface. The CST was determined using a Triton CST Apparatus (Type 165) with a CST paper of size 7×9cm. SRF tests were performed using a Buchner funnel with a Whatman No. 1 qualitative filter paper. A 45kpa of vacuum suction was applied. Value of SRF was calculated using the gradient of linear plot of filtrate (V) against the time over filtrate (t/V). Metals and anionic ions in dried sludge were determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS Advantage). Humic acids (in terms of total organic carbon) were determined by TOC-V CSH (Shimadzu).
Zeta potentials of raw and conditioned sludge were monitored by a zeta potential analyser (ZC-2000).

[Table 1 here]

Two polymers, namely FO-4140 PWG and Magnafloc LT-25 were provided by the Ballymore Eustace Water Treatment Works. The polymers were initially prepared in 0.5% stock solution using nanopure water and then further diluted in a 0.01% solution and used after 24h. The basic characteristics of polymers are presented in Table 2.

[Table 2 here]

A common jar-stirring device of Triton–WRC type 131 was used to mix the sludge. Sludge samples of 100mL in a series of 250mL beakers were used in the experiments. In single polymer conditioning the pre-calculated dose of polymer was added to sludge sample and mixed immediately for promoting the coagulation for 10s at 100rpm. Thereafter, the sample was subjected for a slow mixture to enhance the flocculation for 60s at 45rpm. In dual polymer conditioning however, the pre-calculated dosage of cationic polymer was first added and mixed for 10s at 100rpm. The anionic polymer was then added and mixed for 10s at 45rpm, followed by another 60s mixture at 45rpm. CST and SRF of conditioned sludge were measured according to the procedure described above. The data were recorded three times and average value was used in this paper.
Raw and conditioned sludge samples were transferred for settling tests in 100mL measuring cylinders (30mm in diameter). Settling rates were thus obtained through these static settling tests by calculating the slopes of the settling curve recorded according to the height of the supernatant-particle/floc interface against settling time.

RESULTS

Capillary Suction Time (CST)

Results of CST tests of single polymer and dual polymer (weight 1:1) conditioned alum sludge are shown in Figure 1. The CST of raw sludge is 96.0s. According to Figure 1, the lowest CST, which indicates the fastest water release, for cationic polymer FO-4140 dosage is 50mg/L and the corresponding CST is 10.3s. Thus the dose of 50mg/L can be considered as optimal dosage. Further increase beyond the optimal dosage cannot bring about the improvement in CST value. Similarly, the optimal dosage of the anionic polymer LT-25 in its single polymer conditioning is 30mg/L and the corresponding CST is 9.8s. Further increase in dosage of this polymer shown in Figure 1 will lead to the increase in CST values (12.8s at 50mg/L), implying the deterioration in sludge dewaterability. It is interesting to note from Figure 1 that the sludge pre-conditioned with the cationic polymer followed by the anionic polymer (weight 1:1) illustrates a good dewaterability with CST of 9.2s at a total polymer dosage of 30mg/L. With regard
to the optimal dose, there is no considerable difference between dual polymer conditioning and single anionic polymer LT-25 conditioning although less dosage can be observed in dual polymer conditioning comparing with the case of the conditioning by cationic polymer FO-4140.

[Fig.1 here]

Figure 2 presents a contour plotting of the results of CST in dual polymer conditioning with FO-4140 dosage in the range of 5-25mg/L while LT-25 dosage of 5-45 mg/L. It can be seen clearly from Figure 2 that there is an admissible low region of CST values in the centre of Figure 2. Any combination in FO-4140 dosages from 8-16mg/L and LT-25 from 15-28mg/L will achieve CST values less than 9.5s. This special dual polymer dosage region can be treated as “optimal region”. The existence of “optimal region” implies that there is optimal ratio between FO-4140 and LT-25 in dual polymer conditioning. The high CST values are observed outside the “optimal region”. For example, the CST is higher than 14.5s if the total dosage of polymers is over 60mg/L. It is proposed that at higher dosage, excess polymer remains in the liquid phase, and the increased viscosity results in the deterioration of dewaterability. [6,7]

[Fig.2 here]

**Specific Resistance to Filtration (SRF)**

Results of SRF tests of single polymer and combined dual polymer (1:1) conditioned sludge are shown in Figure 3. The SRF of raw sludge is $7.3 \times 10^{12}$ m/kg. By inspecting
Figure 3, the optimal cationic polymer FO-4140 dosage is 50mg/L and the corresponding SRF is $0.81 \times 10^{12}$ m/kg. Overdose was found on further increase of the SRF value. The optimal anionic polymer LT-25 dosage is 30 mg/L and the SRF is $1.16 \times 10^{12}$ m/kg. In case of dual polymer conditioning, it is seen from Figure 3 that the optimal total polymer dosage is 30 mg/L and the SRF was $1.06 \times 10^{12}$ m/kg. There was no significant change of SRF on further increase of polyelectrolyte dosage in 30-40 mg/L, which is similar with the results of CST and implies the “optimal range” for dual polymer conditioning. However, significant increase of SRF is observed at the dual polymer dose over 40 mg/L. The increase of SRF has been identified due to the clogging of filter medium (during SRF measurement) caused by the excess polymer. [8]

The results of SRF tests of the polymer FO-4140 ranged from 5-25mg/L combined with polymer LT-25 ranged from 5-45mg/L are shown as a contour plotting in Figure 4. It can be seen that the lowest SRF region occurs in the combined doses of FO-4140 from 7-16mg/L and LT-25 from 14-26mg/L, where the SRF of less than $1.0 \times 10^{12}$ m/kg can be achieved. Again, the combined dual polymer dose region to produce the lowest SRF values can be considered as “optimal region”. Any combination of dual polymer dosages outside the optimal region by either increasing or decreasing the dosage will cause the deterioration of sludge dewaterability by exhibiting the high values of SRF. For example, SRF will exceed $5.1 \times 10^{12}$ m/kg when the total polymer doses are over
60mg/L as shown in Figure 4. On the contrary, SRF will be higher than $1.1 \times 10^{12}$ m/kg when the total polymer doses are less than 20mg/L.

[Fig. 4 here]

**Settling Characteristics**

The height (in mL as convenient) of sludge-water interface as a function of time at dosage of various amount of LT-25 in 90min settling is shown in Figure 5. It can be seen obviously that the raw alum sludge is difficult to settle, with only insignificant change of the height of interface during the settling period. However, polymer dosing can significantly improve sludge-water separation by forming flocs and thus accelerating the settling. Figure 5 shows that faster settling is observed with increased polymer dose. However, settling characteristics are very similar after 30min settlement when dosages are over 15mg/L. In particular, it is difficult to distinguish the settling characteristics at the LT-25 dosages of 30mg/L, 35mg/L and 45mg/L. Nevertheless, by considering the minimal polymer dosage which brings about similar settling characteristics in a number of polymer doses, it is reasonable to accept that the optimal dosage of LT-25 is 30mg/L. Actually, settling characteristics of polymer conditioned sludge has been extensively studied and evidenced by the deteriorative settlement in overdose range due to the large but less compacted flocs and increased viscosity in the settling environment. However, this appears not to be the case in the current study. In fact, settling behaviour may be controlled by many factors since the flocs are of different size, of different degree of compactness and are interconnected to form the
complicated aggregate structures. According to the viscosity model developed by Bache and Papavasilopoulos, \(^7\) increases in viscosity in the overdose range may be attributed to the excess polymer or the saturation adsorption of polymer.

[Fig. 5 here]

Figure 6 illustrates the comparative results of settling behaviour of the sludge dosed respectively by polymer FO-4140 (50mg/L), polymer LT-25 (30mg/L) and dual polymer FO-4140 and LT-25 (30mg/L) at dose ratio 1:1. The individual dosage represents the optimal dose for single and dual polymer conditioning. It is seen from Figure 6 that the same trends of settling behaviour can be observed. Calculated settling rates for polymer FO-4140 conditioning, polymer LT-25 conditioning and dual polymer conditioning are 3.1cm/min, 3.3cm/min and 3.3cm/min, respectively, which indicate little difference between settling behaviour.

[Fig. 6 here]

DISCUSSION

Validity and Mechanisms of Dual Polymer Conditioning

It has been shown from Figures 2 and 4 that the combined use of a cationic polymer followed by an anionic polymer, both in a specific range of dosage, may produce excellent flocculation in alum sludge conditioning when the dewaterability was gauged by lowest CST and SRF. However, it is evident from Figures 1 and 3 that the dual
polymer conditioning of alum sludge has not exhibiting considerable advantage over the single polymer conditioning with regarding to achieving further reduction of CST and SRF. This has been confirmed by the settling behaviour of the single and dual polymer conditioned sludge. As illustrated in Figure 6, the similar settling behaviour was observed at the “optimal dosage” of single and dual polymer conditioning. The only advantage of dual polymer conditioning, if any, lies in the reduced total polymer dosage compared with that of the cationic polymer FO-4140 conditioning (Fig. 1 and 3). However, this advantage seems very weak when increased cost and administrative work of the installation, operation and control process in dual polymer conditioning strategy are considered. Thus, the current study supports the conclusion obtained by Ayol et al. [4] that dual polymer conditioning of water treatment sludge (alum sludge in current study) cannot be recommended unless other polymer combinations can be identified and the clear advantages can be exhibited.

Regarding the conditioning mechanism, it is noted from Figures 1 and 3 that, in single polymer conditioning, the anionic polymer (LT-25) shows clearly lower dosage to achieve the lowest CST (Fig. 1) and SRF (Fig. 3), suggesting better dewaterability than that of using cationic polymer (FO-4140). Results of zeta potential measurement indicated that there were insignificant changes of zeta potential (compared with the initial value of raw alum sludge of -7.9mV) with polymer dosages for single and dual polymer conditioning strategies. At the optimal polymer dosages, the zeta potentials were -4.5mV (for FO-4140), -8.4mV (for LT-25) and -5.8mV (for combined use of FO-
4140 and LT-25), respectively. Thus, it is reasonable to believe that the polymer charge
is less important and charge neutralization seems not the major conditioning mechanism
in the current study since the origins of the fine sludge particles and colloids exhibited
negative charges in their surface groups (see Table 1). This view agrees with that
reported by Ayol et al. [4] and Lai and Liu [10] who claimed a less importance of polymer
charge in dual polymer conditioning and considered charge neutralization being not the
dominant mechanism in the alum sludge co-conditioning. However, the view disagrees
with the results indicating that the charge neutralization appears to be an important
consideration in an alum sludge dewatering and moisture content. [11] Nevertheless, it
should be noted that, due to the differences in the quality of the source water and the
varied treatment chemicals and processes in practice, alum sludge can significantly vary
in Al and other mental ions in their characteristics. [12-13] More importantly, Bugg et al.
[14] have demonstrated that, for alum sludge conditioning, anionic polymers were
somewhat superior to non-ionic polymer and significantly superior to cationic agents.
They explained that, at close ranges, the chemical forces often overwhelm the
electrostatic force of either attraction or repulsion. Therefore, it is not surprising to
observe that negatively charged particles are often found to be best aggregated by
negatively charged polymers. [14]

Keeping in mind of the above, the inter particle bridging may play a leading role in
alum sludge conditioning. Therefore, the mechanism of polymer LT-25 conditioning
can be proposed as inter particles or primary flocs bridging. [1] Since there are Al$^{3+}$,
Fe$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ ions in the sludge (see Table 1), the anionic polymer (LT-25) could be adsorbed on the surface of alum sludge by the physical and chemical force such as Van der Waals force and H-bonding and by a ligand or anion exchange;\textsuperscript{[15]} then further flocculation was enhanced by the bridge action of polymer. This may include reaction and connection of improved loops, trains and tails on surface particles and thus the enhanced flocculation can be completed.\textsuperscript{[16-18]} However, in this study, cationic polymer was found to have a better ability to capture fine dispersed particles than anionic polymer. Measurements of supernatant turbidities after 30 min settling of single polymer conditioning show that the turbidity ranged from 1.19 to 2.22 NTU when single cationic polymer FO-4140 was used and turbidity ranged from 2.12 to 3.25 NTU while anionic polymer LT-25 was adopted. The cause of this result may be difficult to address without any further measurement in floc and suspension characteristics such as floc size, density, compactness and residual of polymer in supernatant etc.

In the process of dual polymer conditioning, although the good dewaterability could be obtained in a wide “optimal range” of each polymer dosage (see Fig. 2 and 4), the fact of the similar behaviour of dual polymer and single anionic polymer (LT-25) conditioning shown in Figures 1 and 3, respectively, can lead to a reasonable understanding that the mechanism of dual polymer conditioning is dominated by inter particle bridging. Although dual polymer conditioning of sewage sludge (biosolids) has been documented as more compact primary flocs being firstly formed with a cationic polyelectrolyte pre-conditioning under charge neutralization function, followed by post-
added anionic or nonionic polyelectrolyte for the purpose of bridging the gaps between the flocs, \cite{2,3,19} this mechanism is not supported by dual polymer conditioning of an alum-based water treatment works sludge in current study. The reasons of different profile in dual polymer conditioning of biosolids and water treatment sludge may be partially due to the fact that the alum sludge contains more solid content with less organic material than activated sludge \cite{20} and thus it exhibits different behaviour than activated sludge when different type of polymer is employed for conditioning. \cite{16} Obviously, more research work on this aspect is desirable.

**Relationship between CST and SRF**

Although CST and SRF are the most commonly used indexes in evaluating polymer dosage in sludge conditioning, results from the literature have shown a discrepancy in their use in gauging optimal dosage. Optimum derived from SRF estimation was reported to be higher than that of CST \cite{7,20} while the optimal dosage evaluated by CST being higher than that from standard SRF was also reported. \cite{21,22} Although an attempt to correlate CST and SRF was made and several findings have been reported, \cite{23,24} there has been a lack to seek the theoretical relationship between the two indexes. In their original CST paper, Baskerville and Gale \cite{25} attempted to obtain a correlation between CST and SRF. Following this route, Kavanagh \cite{26} and Lee and Hsu \cite{27} had made theoretical predictions of correlation between CST and SRF, however, it seemed that there has been no direct relationship between the two indexes although some researcher
plotted CST against SRF directly and found that CST has linear relationship with SRF.

In the original SRF theory, the rate of release of the filtrate volume \( V \) with time \( t \) can be written:

\[
   t = \frac{\mu \cdot SRF \cdot C_s \cdot V^2}{2A^2 P_t} + \frac{\mu \cdot R_m}{AP_t} V \tag{1}
\]

in which \( A \) is the filtration area, \( P_t \) is the total pressure drop, \( C_s \) and \( \mu \) are respectively sludge solid concentration and the dynamic viscosity of the filtrate. \( R_m \) refers to the resistance per unit area of filter medium. The period required to increase the volume of filtrate from volume \( V_1 \) to \( V_2 \) is thus given by:

\[
   t_2 - t_1 = CST = \frac{\mu \cdot SRF \cdot C_s}{2A^2 P_t} (V_2^2 - V_1^2) + \frac{\mu \cdot R_m}{AP_t} (V_2 - V_1) \tag{2}
\]

For pure water \( C_s \) is zero so that:

\[
   t_2 - t_1 = CST_{water} = \frac{\mu \cdot R_m}{AP_t} (V_2 - V_1) \tag{3}
\]

Combining Equations 2 and 3 and defining \( CST' \) as the difference between the values obtained for the sludge and pure water yield:

\[
   CST' = CST - CST_{water} = \frac{\mu \cdot SRF \cdot C_s}{2P_t A^2} (V_2^2 - V_1^2) \tag{4}
\]

When Equation 4 is used in the case of constant sludge solid concentration, the relationship between these two indexes can be determined by log-log plotting of \( \mu \cdot SRF \) against \( CST' \). Figure 7 illustrates the plot of the SRF and CST data from all the single
and dual polymer conditioning derived from the current study. As can be seen from the figure that the \( \log CST' \) and the \( \log(\mu \cdot SRF) \) exhibit a considerable good relationship, with correlation coefficient of 0.70. It is believed that some errors that hinder the high correlation may result from the wide range of polymer doses and different polymers in single and dual polymer conditioning. It is worth noting that sludge is a particularly difficult material to characterize in a quantitative manner. To identify the optimal dosage in polymer conditioning is also difficult since the formation of flocs is a complex physico-chemical process. Certain discrepancy in evaluating the optimum dose between different approaches such as CST and SRF reflects the complexity. Nevertheless, seeking more accurate correlation between CST and SRF is encouraged from both academic and practical points of view.

[Fig. 7 here]

CONCLUSIONS

The study compared the effectiveness of a cationic polymer FO-4140 and an anionic polymer LT-25 for conditioning of an alum-based water treatment sludge in single and dual polymer methods of conditioning. The results have demonstrated that both the cationic polymer and the anionic polymer can be solely used for an Irish alum sludge conditioning. However, for the current study using the sludge with SS of 2,985 mg/L, polymer LT-25 exhibits the advantage of less “optimal dosage” of 30mg/L than that of 50 mg/L when polymer FO-4140 is adopted. In the process of combined use of these two polymers (weight 1:1) in terms of the dual polymer conditioning, it has been
demonstrated that there exists a wide “optimal region” of total polymer dosage in dual conditioning. Any combination of these two polymers with the dose of FO-4140 from 7-16 mg/L and the dose of LT-25 from 14-28 mg/L will lead to good dewaterability evaluated by CST and SRF. However, dual polymer conditioning does not exhibit considerable advantage in achieving further reduction of CST and SRF with comparison of single polymer conditioning. Thus, considering the realization of dual process (cost and administration) such dual conditioning strategy is not recommended unless in a specific situation. With regard to the polymer conditioning mechanism, this study supports the view that for alum-based water treatment sludge, inter particle bridging may be the dominative mechanism and the charge neutralization plays a less important role in the conditioning process. In addition, an attempt to seek theoretical correlation between CST and SRF has been made in this study and the results showed that the correlation between CST and SRF has a considerable good agreement with linear relation between $\log(CST - CST_{water})$ and $\log(\mu \times SRF)$.

**ACKNOWLEDGEMENT**

The first author, Dr W. Ma, would like to thank the University College Dublin for providing his visiting scholarship via Strategic Initiative Fund.
REFERENCES


Table 1  Properties of alum sludge used in this study

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Table 2  Properties of polymers used in this study

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Figure caption

Fig. 1  CST of sludge as a function of polymer dosage in single and dual polymer (weight 1:1) conditioning

Fig. 2  Contour plotting of CST in dual polymer conditioning (addition of cationic polymer FO-4140 followed by anionic polymer LT-25)

Fig. 3  SRF of sludge as a function of polymer dosage in single and dual polymer (weight 1:1) conditioning

Fig. 4  Contour plotting of SRF in dual polymer conditioning (addition of cationic polymer FO-4140 followed by anionic polymer LT-25)

Fig. 5  Positions of sludge-water interface as a function of settling time at various dosages of anionic polymer LT-25

Fig. 6  Height of sludge-water interface as a function of settling time of sludge conditioned with single and dual polymers at specific dosage

Fig. 7  Relationship between SRF and CST
Fig. 1

Fig. 2
Fig. 5
LT-25 of 30 mg/L
FO-4140 of 15 mg/L + LT-25 of 15 mg/L
FO-4140 of 50 mg/L

Fig. 6

\[ y = 1.3439x - 16.048 \]
\[ R^2 = 0.6971 \]

Fig. 7

\[ y = 1.3439x - 16.048 \]
\[ R^2 = 0.6971 \]