EFFECTS OF DUAL POLYMER CONDITIONING
ON SLUDGE DEWATERING

by

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ON SLUDGE DEWATERING

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ABSTRACT

The sludge dewatering has been known as one of the most expensive and hard to handle processes in water and wastewater treatment. Conditioning improves the dewaterability characteristics of sludges by enhancing the flocculation. Alum sludge can be produced from many different water treatment systems with alum. Alum sludges have been recognized as difficult to dewater due to the containing 40 per cent bound water, and are often conditioned with polymers prior to dewatering. In recent years, there have been several studies on dual polymer systems to improve the flocculation of particles in water and wastewater treatment processes.

Dual conditioning leads to an improvement in the sludge dewaterability. In dual conditioning, the better dewaterability can be achieved by using same or less amount of polymer than that of single conditioning. Dual conditioning increase the solid content of the sludge cake, and enhance the solids capture and so reduce the blinding of the filter media.

Rheology is known a direct proportionality relationship between shear stress and shear rate. This simple Newtonian behavior is not applicable for sludges. The conditioned sludges show a non-Newtonian behavior (pseudo-plastic behavior). The rheological measurements are very useful in understanding wastewater treatment performance. The data obtained from rheological measurements defined the optimum dose for sludge conditioning. Stronger floc formation is indicated from the initial yield stress (initial shear stress). Stronger floc formation is not desirable for good dewaterability due to the stronger flocs tend to hold more trapped water between the floc parts in dewatering processes.

This study investigates the effect of dual conditioning on sludge dewaterability and the rheological behavior of the conditioned alum sludges. Based on the results of this study, dual conditioning leads to an improvement in the dewaterability of sludges. The best sludge dewaterability was obtained by adding anionic polymer first and cationic second.

ÖZET

Su ve atıksu arıtma tesislerinde oluşan çamurun susuzlaştırılması günümüzde halen en pahalı ve zor proseslerden biri olmaya devam etmektedir. Çamur susuzlaştırılmasında uygulanan kimyasal şartlandırma, çamurun yumaklaşma kabiliyetini arttırarak daha kolay susuzlaştırmayı sağlar. Arıtma çamurları içerisinde alum çamurları, içerdiği bağlı su miktarının yaklaşık olarak % 40 olmasından dolayı susuzlaştırılması en zor olan çamurlardan biridir ve mekanik olarak uzaklaştırılması zordur. Bu nedenle, alum çamurlarına susuzlaştırma öncesi genellikle kimyasal şartlandırma uygulanır.

Son yıllarda yapılan çalışmalarda ikili şartlandırmanın tekli şartlandırmaya göre bir takım avantajları olduğu görülmüştür. Tekli şartlandırmaya göre ikili şartlandırmada daha iyi susuzlaştırabilirlik elde edilebilmektedir. İkili şartlandırma ile tekli şartlandırmada elde edilen optimum doz değerinden aynı veya daha az miktarda polimer ilavesiyle sudaki partiküllerin daha iyi tutulması sağlanarak, çamur kekinin katısının artması sağlanır.

Sıvılarda kayma gerilmesi, hız gradyantı ve dinamik viskozite arasında direk bir ilişki bulunmaktadır. Ancak çamurun sıvı fazı, Newtonian bir akış sergilerken, çamurun katı fazı non-Newtonian bir akış gösterir. Bu durum çamurun reolojik açıdan karakterize edilmesini zorlaştıran parametrelerden bir tanesidir. Ancak reolojik test sonuçları bize çamurun atıksudaki davranışı hakkında fikir verebilmektedir. Bu veriler bize atıksu arıtma verimini inceleme fırsatı sağlar. Örneğin, güçlü flok oluşumu, başlangıç akma gerilmesi değerinden belirlenebilir. Güçlü floklar, bünyesinde daha fazla miktarda suyu tuttuğundan iyi bir susuzlaştırma için tercih edilmemektedir.

Bu çalışmada ikili şartlandırmanın alum çamuru susuzlaştırma üzerine etkisi ve rheolojik davranışları incelenmiştir. Çalışma sonucuna göre, ikili şartlandırmanın tekli şartlandırmaya oranla susuzlaştırmayı iyileştirdiği görülmüştür. İkili polimer kombinasyonları içerisinde en iyi susuzlaştırma verimi anyonik polimer üzerine katyonik polimer ilavesiyle sağlanmıştır.

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Symbol	Explanation	Units used
A	Attraction forces	kJ/mol
CST	Capillary suction time	s
DMAEA	Dimethyl-aminoethyl-acrylate	
DMAEA.MeCI	Dimethyl-aminoethly-acrylate-methylchloride	
DMAEM	Dimethyl-aminoethly-methacrylate	
DTC	Dimethyl dithiocarbamate	
G	Mixing energy	1/s
HMW	High molecular weight	g/mol
LMW	Low molecular weight	g/mol
MAD	Mesophilic aerobically digested biosolid	
n	Empirical constant	
R	Repulsion force	kJ/mol
PAA	Polyacrylic acid	
S	Summation of curves A and B	kJ/mol
t	Mixing time	s
TAD	Thermophilic aerobically digested biosolid	
TMT	Trimercapto-s-triazine	
w/v	Weight/volume	kg/L
τ	Shear stress	Pa
μ	Viscosity	cps
μm	Micrometer	μm

η	Viscosity of suspension	cps
η_0	Viscosity of solvent	cps
φ	Volume fraction	
τ_0	Yield stress	Pa

INTRODUCTION

The sludge dewatering has been known as one of the most expensive and hard to handle process in water and wastewater treatment. Safe and economic disposal of sludge can be achieved by reducing its water content to the manageable levels.

Dewatering characteristics of sludges are affected by many factors including particle size of sludges, water distribution, solid content, structure and the composition of the flocs, type and ionic structure of the polymers and mixing intensity.

Conditioning improves the dewaterability characteristics of sludges by enhancing the flocculation. Polymers are commonly used for sludge conditioning to improve sludge dewaterability. Conventionally, a single polyelectrolyte is used in sludge conditioning. In recent years, there have been several studies on dual polyelectrolyte systems to improve the flocculation of particles in water and wastewater treatment processes.

Alum sludges have long been recognized as difficult to dewater. They are often conditioned with polymers prior to dewatering. In recent years, polymers have become a primary choice in the sludge dewatering process. Good control of polymer dosage is very critical in sludge conditioning, since overdosing will increase the operation cost while decreasing the sludge dewaterability.

Recent studies on sludge conditioning show that dual conditioning leads to an improvement in the sludge dewaterability. In dual conditioning of sludges, better dewatering properties can be achieved using same or less amount of polymer than used in single conditioning. Dual conditioning increase the solid content of the sludge cake, and enhance the solids capture and so reduce the blinding of the filter media. Stronger and denser flocs can be produced in dual conditioning.

Rheology is known as a direct proportionality relationship between shear stress and shear rate in a fluid. This simple Newtonian relationship is not applicable for sludges. The viscous characteristic of sludge is non-Newtonian and modelled in the literature by using

the pseudoplastic or Bingham plastic rheology models. Sludges from water and wastewater treatment plants are recognize as displaying thixotrophic behavior (reduced viscosity with increasing shear).

This study investigates the effect of dual conditioning on sludge dewaterability and the rheological behavior of the conditioned alum sludges. The dewaterability of sludge was determined by measuring filterability in terms of capillary suction time. The rheological behavior of sludges was determined by evaluating the relationship between shear stress and shear rate.

2. LITERATURE REVIEW

2.1. Sludge Conditioning

2.1.1. The Types and Characteristics of Sludge

Sludge is a concentrated dispersion of particles, usually with a wide range of particles. The interactions of these particles, both with each other and with soluble constituents, have a great importance in determining the properties of the sludge (Gregory, 1983). The characteristics and composition of sludges show great variations according to the differences in operations and processes used in wastewater treatment plants. Sludge resulting from wastewater treatment operations and processes is usually in the form of a liquid or semisolid liquid. Sludge typically contains from 0.25 to 12 per cent solids by weight, depending on the operations and processes used (Tchobanoglous and Burton, 1991). The big portion of these sludge solids is organic in nature (volatile solids). The sludge does not usually have any commercial value. Sludge volume has been increased as a result of extended sewerage and advanced wastewater treatment. Successful sludge management requires a through understanding of processes used in sludge treatment beginning from sludge production to its ultimate disposal. The disposal of sludge is difficult and expensive, often requiring over 50 per cent of the operating budget for the wastewater treatment plant. All organic sludges require a special form of treatment. Common sludge treatment processes include thickening, stabilization, conditioning and dewatering. The ultimate disposal of sludge is facilitated by removing the liquid portion. This process is called as sludge dewatering.

Alum sludge can be produced from many different water treatment systems with alum, commonly name used for aluminum sulphate ($Al_2(SO_4)_3.18H_2O$), as the primary coagulant. Alum sludges have been recognized as difficult to dewater due to their high bound water content of 40 per cent. They are often conditioned with polymers prior to dewatering (Zhao, 2004). Site experiences have linked difficulties in dewatering and increased polymer demand with the rising proportion of alum hydroxide in the sludge

(Nielsen et al., 1973). Alum sludge has a gelatinous appearance, and does not show a resistant to shear effect. The reaction with alum and water is given below.

$$Al_2(SO_4)_3.14\ H_2O + 6HCO_3^- \rightarrow 2\ Al(OH)_3 + 3SO_4^{2-} + 6CO_2 + 14\ H_2O$$

The properties of alum sludge are given Table 2.1. (Kocakulak, 2004). The characteristics of alum sludge depending on the solid content are given in Table 2.2. (Williams and Culp, 1986).

Table 2.1. The typical properties of alum sludge (Kocakulak, 2004)

Parameters	Concentration
Total solid, %	0.1-27
Volatile suspended solid, %	10-35
Suspended solid, %	75-99
pH	5.5-7.5
BOD, mg/L	30-6000
COD, mg/L	500-27000
Aluminum, % (on dry solid basis)	4-11
Ferrous, % (on dry solid basis)	6.5
Manganese, % (on dry solid basis)	0.005-5
Arsenic, % (on dry solid basis)	< 0.04
Cadmium, % (on dry solid basis)	<0.005
Heavy metals, % (on dry solid basis)	< 0.03
Total Kjeldahl Nitrogen, mg N/L	0.7-1200
Phosphate, mg P/L	0.3-300

Table 2.2. The characteristics of alum sludge depending on the solid content (Williams and Culp, 1986)

Solid content, %	Sludge Characteristic
0-5	liquid
8-12	soft, moderate
18-25	hard
40-50	extremely hard

2.1.2. Factors Effecting Conditioning

Sludge dewaterability characteristic take an important role in the selection of the optimal dewatering method. Many characteristics are reported to influence the dewaterability of sludges such as particle size distribution, bound water content, viscosity, structure and the composition of the flocs (Çetin and Erdinçler, 2004).

2.1.2.1. Particle Size. The particle size is the most important factor effecting the dewaterability of sludge. The average particle decreases as the surface area of sludge increase. Particle size is directly influenced by prior treatment and the sludge sources (Spellman, 1997). An important feature of a solid colloid in water is that the solid particles will not settle by the force of gravity. Colloids have an extremely large surface area per unit volume of the particles, means that they have a large specific surface area. The large surface area causes the increasing the attraction of water to the particle surface due to the more adsorption sites (tend to adsorb substances from the surrounding water), the greater electrical repulsion between sludge particles due to a larger area of negatively charged surface and the increasing frictional resistance to the movement of water .

Particles can be classified due to their origin, Steel and McGhee (1979) classified the particles caused turbidity due to their particle size that range from 50 μm or larger. According to the Stokes' law, the minimum particle size should be 50 μm to settle under the influence of gravity alone. The smaller particles will remain in suspended form for very long times. For this reason, coagulation is used for removal of colloidal material. The most

important property for the characteristic of particles of colloidal dimension is the ratio of the surface area to mass. This property determines the stability of colloidal suspension. This situation is clearly apparent from Table 2.3. Table 2.3. lists a number of materials and organisms with their size and an indication of the time needed for these particles to settle vertically though one meter of water at 20°C under the influence of gravity alone according to Stokes' law.

Table 2.3. Settling time for various particles (Water Treatment Handbook, 1991)

Particle diameter, μm	Type of particle	Settling time through 1 m of water	Specific area, m^2/m^3
10^4	Gravel	1 second	6.10^2
10^3	Sand	10 seconds	6.10^3
10^2	Fine sand	2 minutes	6.10^2
10	Clay	2 hours	6.10^2
1	Bacteria	8 days	6.10^2
10^{-1}	Colloid	2 years	6.10^2
10^{-2}	Colloid	20 years	6.10^2
10^{-3}	Colloid	200 years	6.10^2

Zhou et al. (2005) studied on the mechanism of digestion effects on dewatering properties of thermophilic (TAD) and mesophilic (MAD) aerobically digested biosolids. Particle sizes were measured using a Malvern Mastersizer 2000 particle analyzer. Sizes of the most particles in TAD biosolids was 0.8 μm. The mean particle sizes of MAD biosolids was 2 μm. They found that thermophilic digestion had more severe and rapid impact on dewaterability than mesophilic digestion. The worsening of dewaterability in TAD digested biosolids was associated with the production of smaller and finer particles, which corresponded to higher demand of polymers in conditioning TAD biosolids.

2.1.2.2. Mixing Intensity. Investigations have shown that polymer conditioned sludges have much improved filtering rates when compared to rates for the sludge in its original state. Werle et al. (1984) reported that the most important parameters are polymer doses,

mixing time (*t*) and mixing energy (*G*) governing high-shear stress in sludge conditioning. They found that several polymer dosage-*Gt* combinations can be used to achieve the same optimal performance. In alum, activated and primary sludges, optimum polymer requirements increase as mixing energy input *Gt* increase. Alum and activated sludge particles exhibit minor deterioration when subjected to a high *Gt*. Primary sludge particles exhibit extensive deterioration when subjected to high *G* values, regardless of mixing time. This problem can be corrected through use of large polymer dosages.

2.1.2.3. <u>Solid Concentration</u>. The optimum polymer dosage for sludge conditioning is directly related to the fraction of fines in the sludge. Mikkelsen and Keiding (2001) reported that the optimum polymer dosage increase with the activated sludge solids concentration both in terms of absolute dosage and dosage per solids content. Optimum polymer dosage is not corresponded to charge neutralization of the activated sludge as the zeta potential remained negative even for considerable over-dosing. Supernatant turbidity prior to conditioning also increased with the solids concentration. Erikkson (1987) also found that no correlation between electrophoretic mobility and conditioner dosage. Mikkelsen and Keiding (2001) suggested that reduction of the colloid fraction is a critical factor in dewatering and not necessarily coincident with charge neutralization.

2.1.2.4. <u>pH</u>. pH affects the surface charge on sludge particles. pH is very important characteristics that determines the type of polymer to be used for conditioning. If the solids conditioned with lime has a high pH, anionic polymers are recommended to use for dewatering processes. On the other hand, if the pH is slightly above or below neutral, cationic polymers are recommended (Spellman, 1997).

2.1.2.5. <u>Water distribution</u>. There is three different types of water can be distinguished according to their physical bonding to the sludge particles. The water types in sludge are shown in Figure 2.1.

The free water content represents the largest part as 70-75 per cent in sludge. It is not influenced by capillary forces. This type of water can be separated by gravity and mechanically, for example by centrifugal forces or filtration. The maximum solids content in the sludge cake, which can be achieved with mechanical dewatering. The capillary water

is kept in the interstice of the sludge particles and micro-organisms in the sludge floc. It is physically bound by active capillary forces. The intracellular water contains the water in cells. It can be removed by thermal processes (Vesilind, 1994).
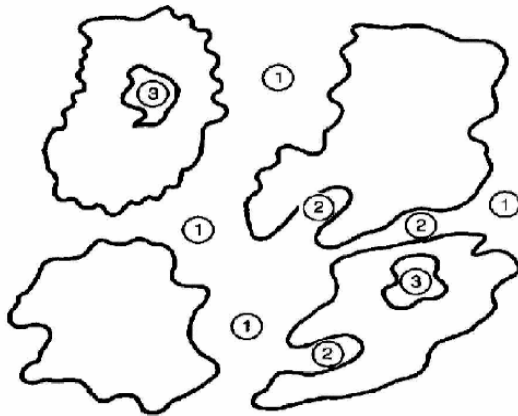
1- Free Water

2- Capillary (Intercellular) Water

3- Intracellular Water

Figure 2.1. Types of water in sludge (Nalco Raw Water/Wastewater Technical Manual, 2006)

2.1.3. Sludge Conditioning with Chemicals

Sludge conditioning has been considered to be accomplished by the processes of coagulation and flocculation. Coagulation is defined as the process that causes a reduction of repulsion force between particles or colloids. When coagulant is added into sludges, the zeta potential is altered thus, allowing the individual particle to agglomerate.

2.1.3.1. Sludge Conditioning with Inorganic Chemicals. The chemicals involved in coagulation are knows as coagulants and/or coagulant aids. The list of the coagulants most commonly used in the processes is given below.

<u>Aluminium Sulfate</u> $Al_2(SO_4)_3$. It is known as alum. It is available in solid and in solution form. It is the most widely used inorganic coagulant. It is used for metals removal, oil-grease separation and water clarification. It is acidic and corrosive.

<u>Ferric Chloride</u> $FeCl_3$. Ferric chloride is one of three iron compounds used in the water treatment, phosphate removal, sludge conditioning and dewatering, trace metals removal, and odor control applications. It is typically sold in solution form. It is available in solution (27-43 per cent of $FeCl_3$) form. Ferric chloride solutions are very acidic and corrosive.

<u>Ferrous Sulfate</u> $FeSO_4$. Ferrous sulphate and lime coagulation is usually less expensive than alum. It is available in dry or liquid form (5-12 per cent). Ferrous sulphate requires alkalinity in the form of hydroxide ion in order to produce a rapid reaction. Hydrated lime, $Ca(OH)_2$, is usually added to raise the pH to a level where the ferrous ions are precipitated as ferric hydroxide. It is used for phosphate removal, trace metals removal, and odor control applications. It is very acidic and corrosive.

<u>Ferrous Chloride</u> $FeCl_2$. It is only available in liquid form (8-14 per cent iron). It is used for phosphate removal, odor control, heavy metals removal, controls toxic sulfide generation in anaerobic digesters, oil-grease removal, and sludge conditioning applications. It is very acidic and corrosive.

<u>Ferric Sulfate</u> $Fe_2(SO_4)_3$. It is available in dry form as granular or as a powder and in solution (10-13 per cent iron) form. It is used for water clarification, decolorization of surface water, sludge conditioning and dewatering, trace metals removal, organics removal (including trihalomethanes), sulfide control, phosphate removal, oil-grease separation and DAF. It is very acidic and corrosive.

<u>Hydroxylated Ferric Sulfate</u> $Fe_5(SO_4)_7(OH)$. It is the newest of the iron salts. It van be used instead of alum. It is available in liquid form. It is very acidic and corrosive.

<u>Aluminium Chloride</u> $AlCl_3$. It is available in solid and in solution form. It is used for metals removal, oil-grease separation and water clarification. It is acidic and corrosive.

Calcium Chloride $CaCl_2$. It is available in dry and liquid form. It is infrequently used for metals removal, organics reduction and water clarification. $CaCl_2$ also has great utility for phosphate removal. It is nonhazardous.

Magnesium Hydroxide $Mg(OH)_2$. It is used for pH control. The sludge level is reduced by using magnesium hydroxide,$Mg(OH)_2$, as a precipitant. It is very safe to handle, contains no heavy metals. It is available as in 50 per cent slurry or solution form. The dissolution rate of slurry form is very slow.

Polyaluminium Chloride (PAC). This describes a wide variety of materials containing more than one aluminum atom in the molecule up to about 13. These materials are typically described by their Al_2O_3 content and basicity. Al_2O_3 ranges from about 8 to 25 per cent and basicity is usually between 50 and 70 per cent for most commercial products. Aluminum chlorohydrate is an example of a PAC. Some manufacturers replace part of the chloride content with silicate or sulfate. Some materials are corrosive. It is only available in solution form.

Sodium Aluminate $Na(AlO_2)$. It is used for color removal, phosphorus removal, lime softening, pH control, and many papermaking applications. It is very alkaline and corrosive. It is available in liquid form.

Precipitants and Other Inorganic Treatment Chemicals. There are numerous chemicals which are used in waste treatment for precipitation and to aid in removal of unwanted matters.

The following is a short list of products used mainly for pH adjustment and buffering:

- Sodium Carbonate (Soda Ash)
- Sodium Hydroxide (Caustic Soda)
- Potassium Hydroxide (Caustic Potash)
- Sulfuric Acid
- Calcium Oxide (Lime)
- Magnesium Oxide

There are several products used for metals precipitation: sodium sulfide, sodium polysulfide, dimethyl dithiocarbamate (DTC), and trimercapto-s-triazine (TMT). DTC and TMT are the most widely used products. These two materials form insoluble complexes with dissolved metals.

2.1.3.2. Sludge Conditioning with Organic Polyelectrolytes. Natural and synthetic materials called as polyelectrolytes have characteristics of both polymer and electrolyte. In recent years, synthetic flocculants as the polymers have replaced inorganic flocculants for the conditioning of sludge. Polymers generate significantly less sludge than inorganics. Inorganic flocculants have been found to comprise as much as 20 per cent of a dewatered sludge on a dry weight basis. Polymers are rarely required in concentrations exceeding one per cent of the sludge on dry weight basis. The pH of the sludge and filtrate does not be changed by the addition of polymers. Therefore, the need for readjustment of pH may be eliminated. Inorganic chemicals can create corrosion and operational problems in the plant, because of being in high pH. Polymers are generally considered more convenient and easier to use than inorganics. Smaller volumes of polymers are required and solution preparation is easily automated for safe operation. Polymers generally form larger and stronger flocs. A major benefit obtained with polymers is a very large increase in floc size. Their larger floc size facilitates dewatering by increasing the release of water and decreasing the overall sludge surface area. This reduces surface drag forces between the sludge particles and the water (Knocke and Zentkovich, 1986). Stronger flocs are more resistant to shear forces. Therefore, flocs are not easily breaking up during processing. Polymers also do not increase the dissolved salt concentration of the separated water. The concentration of salts in the filtrate is increased with inorganic chemicals. It could potentially cause operational problems in the treatment operations due to the recycling of the filtrate back to the front of the plant.

In spite of the numerous advantages of polymeric flocculants, inorganic conditioning chemicals are still often used for economy in chemical cost. However, Sligar estimated that the cost for treatment with polymers would be less than 50 per cent of the cost for a ferric chloride-lime treatment process on a filter press at his plant. In addition, polymers can offer many significant economies in final disposal of dewatered sludge (Sligar, 1984).

<u>Polymer Structure and Properties</u>. Synthetic polymers are synthesized by the polymerization of monomers. The monomers in the polymerization constitute the repeat units, for example, acrylic acid is polymerized into polyacrylic acid. A polymer can either be linear, branched or cross-linked. In water treatment applications, linear and branched polymers are most frequently encountered. Cross-linked polymers are usually only partially soluble in water. If the polymer is synthesized with more than one kind of monomer, it is called a copolymer. The monomer units in a copolymer can be either be randomly distributed, distributed in blocks or distributed such that one of the monomers is grafted in chains onto the backbone of the other monomer chain. The solution properties and the surface chemical properties are very sensitive to which category a copolymer belongs.

The polarity of the monomer units is a convenient basis to categorize non-biological polymers:

- non-polar polymers such as polystyrene and polyethylene,
- polar, but water-insoluble polymers, such as polymethyl methacrylate,
- water-soluble polymers, such as polyoxyethylene and polyvinyl alcohol,
- ionizable polymers or polyelectrolytes, such as polyacrylic acid.

A polymer can form a random coil, an extended configuration or a helix. For synthetic polymers, the random coil is the most common figure. Polyelectrolytes, where the monomer units are charged, can under certain circumstances form stiff rods. Polyelectrolytes in solution have many applications and are used technically as thickeners, dispersants, flocculation aids, etc. Synthetic polymers can be classified according to the ionic character of the polymer: nonionic, anionic and cationic (Holmberg et al., 2003).

Most synthetic polymers are based on polyacrylamide and its derivates. Polyacrylamide is essentially nonionic and synthesized by acrylamide monomers, and the ionic character is varied by copolymerization with other monomers. Polyacrylamide is a very hydrophilic polymer which is insensitive to the addition of salts. This polymer is used to flocculate solids through bridging due to having high affinity to surfaces. The structure of acrylamide and polyacrylamide given in Figure 2.2.

$$CH_2 = CH \qquad\qquad CH_2 - CH - CH_2 - CH - CH_2$$
$$\qquad | \qquad\qquad\qquad\qquad\quad | \qquad\qquad\quad |$$
$$\qquad C = O \qquad\longrightarrow\qquad\quad C = O \qquad\qquad C = O$$
$$\qquad | \qquad\qquad\qquad\qquad\quad | \qquad\qquad\quad |$$
$$\qquad NH_2 \qquad\qquad\qquad\qquad\quad NH_2 \qquad\qquad NH_2$$

Acrylamide   Polyacrylamide
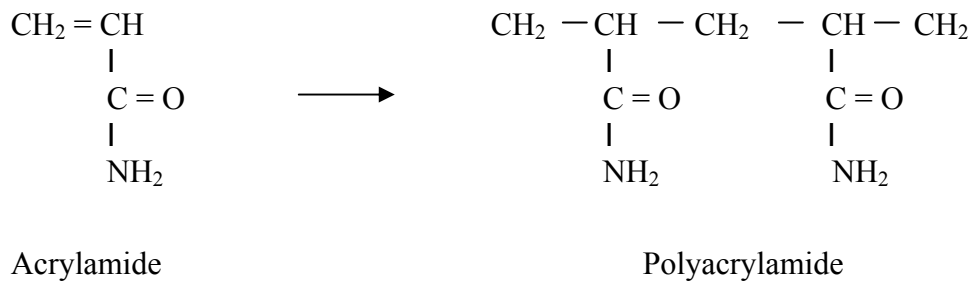
Figure 2.2. The structure of acrylamide and polyacrylamide

Anionic polymers are negatively charged and can be manufactured with a variety of charge densities. Polyacrylate and anionic polyacrylamides are essentially anionic. Anionic polyacrylamides may be prepared by copolymerization of acrylic acid with acrylamide, or by partial hydrolysis of polyacrylamide. This is the most common type of synthetic polymer. However, polyacrylate is the copolymer of acrylic acid and sodium acrylate. Intermediate charge densities are usually the most useful. Anionics are normally used for bridging to flocculate the solids. The acrylamide based anionic polymers with very high molecular weights are very effective to flocculate the solids. However, anionic polymers may be capable of flocculating large particles, but a residual haze of smaller colloids will almost remain. The structure of polyacrylate and polyacrylamide are given in Figure 2.3.

Cationic polymers are copolymers of acrylamide and a cationic monomer, the type of cationic monomer being variable depending on the application. The cationic polymers are positively charged with a wide range of charge densities and molecular weights. The commonly used cationic monomers are dimethyl-aminoethly-methacrylate (DMAEM), dimethyl-aminoethyl-acrylate (DMAEA) and dimethyl-aminoethly-acrylate-methylchloride (DMAEA.MeCI) (Water Treatment Handbook, 1991). The structure of typical cationic polymer is given in Figure 2.4. High molecular weight cationic polymers can be thought as double acting because they act in two ways: charge neutralization and bridging.

Acrylic acid   Sodium acrylate

Polyacrylate

Anionic polyacrylamide
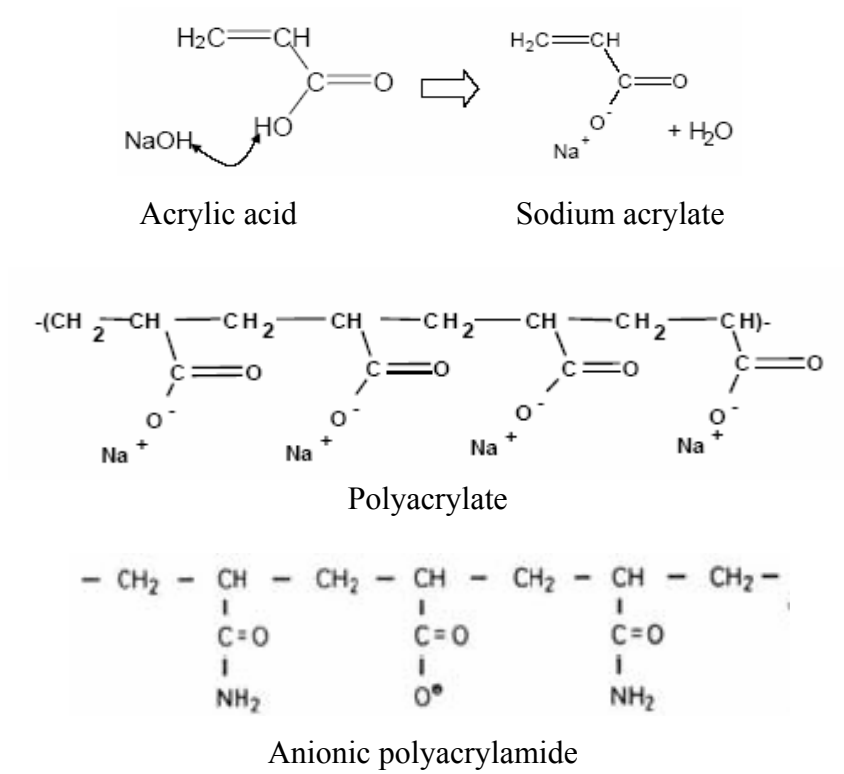
Figure 2.3. The structure of polyacrylate and anionic polyacrylamide polymers

DMAEA.MeCl

DMAEA.MeCl   Acrylamide
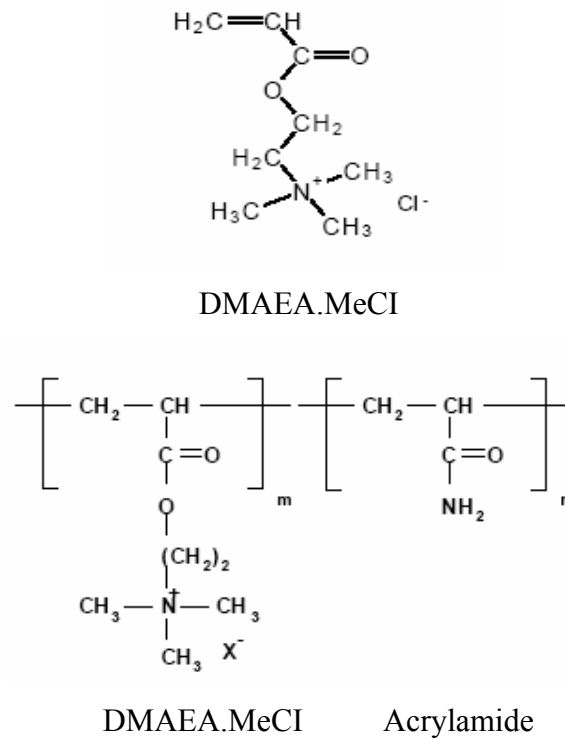
Figure 2.4. The structure of typical cationic polymer

General Types of Polymers and Production Units

Dry, Powdered or Granular Polymers. The majority of these polymers are made overseas in Europe or Japan although there are now some domestic manufacturers as well. These polymers benefit from the fact that they are essentially 100 per cent active. Dry polymers are difficult to wet and dissolved rather slowly. They require special feed equipment for making up large amounts of diluted polymer. Typically, these polymers are put into solution by the use of automated dilution systems. Figure 2.5. illustrates the typical dry polymer preparation scheme.

Dry polymers are very sensitive to moisture. They should be stored in very dry location and kept free from moisture. Dry polymers are also limited by viscosity, so the upper range is about 1 to 2 per cent. Dry polymers can be nonionic, anionic or cationic and can have a wide range of charge densities. They are typically high molecular weight materials (MW > 1 million).

Dry polymer feeder   Mixing tank   Feeding tank
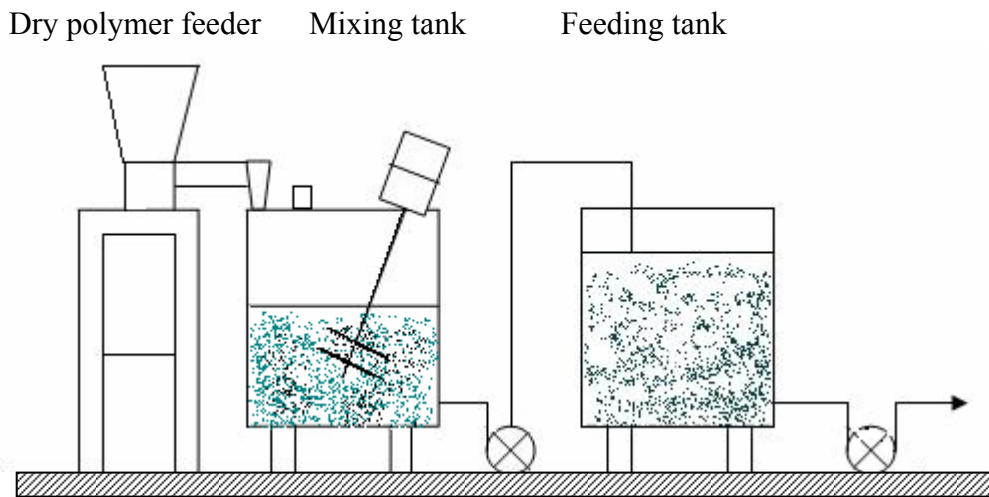
Figure 2.5. Typical dry polymer preparation scheme.

Liquid or Solution Polymers. Solution polymers are solutions of water soluble polymers in water. They often preferred to dry polymers because they are more convenient. They benefit from the advantage of being relatively easy to put into dilute solution. They do not require sophisticated equipment. However, high molecular weight polymers are limited by viscosity, so they are frequently very dilute and very viscous. Solution polymers are

typically cationic. They have a wide variety of charge densities and molecular weights. Active ingredients can vary from a few per cent to 50 per cent.

Emulsion Polymers. Emulsion polymers are very easy to put into solution. They allow very high molecular weight polymers to be purchased in convenient liquid form. Emulsion polymers are usually packaged as 20-30 per cent active ingredients. Emulsion polymers can be nonionic, cationic or anionic. They can have a wide variety of charge densities and are usually medium to high molecular weight. Their low bulk viscosity and liquid form makes them very easy to handle, especially in automated systems. They can be diluted by a variety of methods ranging from simply pouring them into the vortex of mixing water to sophisticated dilution systems which require very little manpower to operate. Figure 2.6. illustrates the typical emulsion polymer preparation scheme.

Dilution levels of these products are limited by viscosity, so the upper limit is usually 2 to 3 per cent. In practice, however, it is usually better to dilute to 0.5 or 1.0 per cent. This permits the full dissolution of the polymer.

Emulsion polymer tank   Mixing tank   Storage tank   Day tank
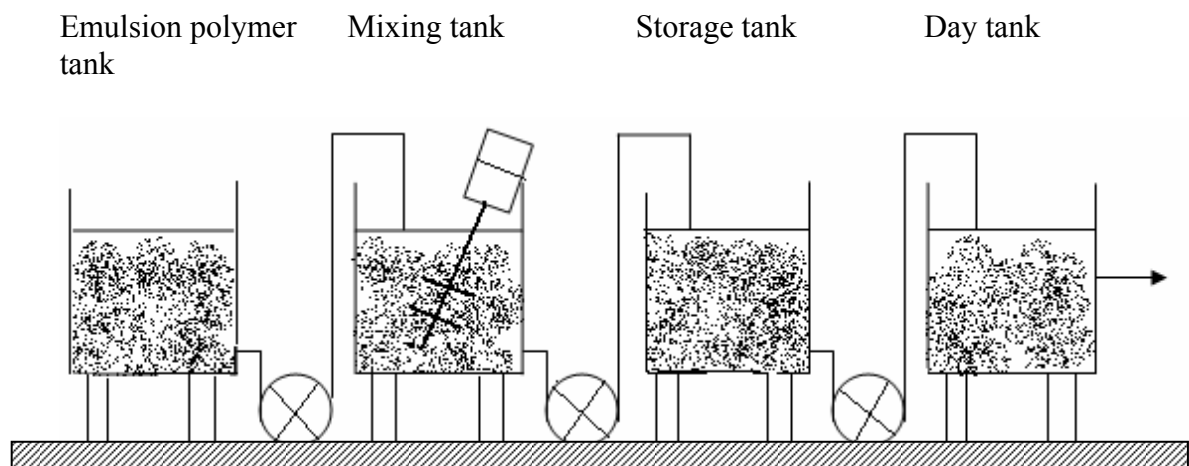
Figure 2.6. The typical emulsion polymer preparation scheme.

2.1.4. Mechanisms of Conditioning

Flocculation occurs by four distinct mechanism: double layer, reduction of electrical charge (charge neutralization), enmeshment (sweepfloc) and interparticle bridging (Moss and Dymond, 2006).

2.1.4.1. Bridging Mechanism. The major mechanism of flocculation of municipal sludges is bridging. This mechanism is characterized by adsorption of a polymer chain to more than one particle.

In the bridging mechanism, the molecular weight of the polymer is important. The higher molecular weights are more effective in flocculation allowing the adsorption on several particles at once. The effects of molecular weight often can not be compensated by dosage. Cole and Singer (1985) reported that a use of cationic polymers with molecular weights greater than $1x10^6$ are most effective for conditioning anaerobic digested sludge. In bridging mechanism, the polymer is strongly adsorbed. The adsorption is promoted by chemical groups having good adsorption characteristics, for example amide groups. Either cationic or anionic groups are used to extend the polymer chain as long as the polymer is of high enough molecular weight for bridging. The cationic polymer added need not to be of a high molecular weight, as long as it adsorbs or precipitates on to particle surfaces and possesses a positive electrical charge at the pH of use. However, the cationic polymer is much more effective to form the larger flocs allowing its cationic sites to bind more than one particle, thus, bridging the system of solid particles. Figure 2.7. illustrates the bridging mechanism.

Bridging is often used in conjunction with charge neutralization to enhance fast settling and/or shear resistant flocs. For instance, alum or a low molecular weight cationic polymer is first added under rapid mixing conditions to lower the charge and allow microflocs to form. Then the small amount addition of high molecular weight anionic polymer provides the bridging between the microflocs. The fact that the bridging polymer is negatively charged is not significant because the small colloids have already been captured as microflocs.
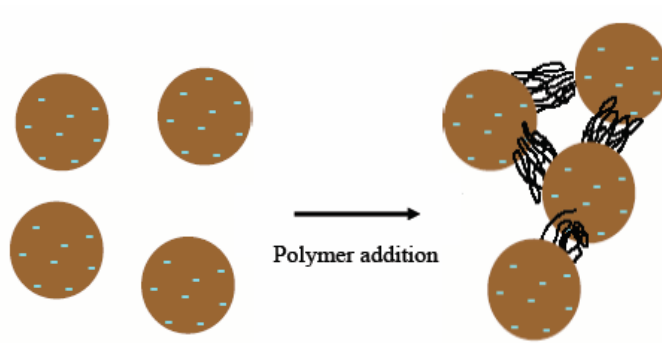
Figure 2.7. Bridging mechanism (Ergin, 2005)

Bridging mechanisms are occurred as following reactions:

Reaction 1. Polymer molecule is attached to a particle surface. If the particle and polymer are of opposite charge, the Columbic attraction will occur.

Polymer   Particle   Destabilized particle
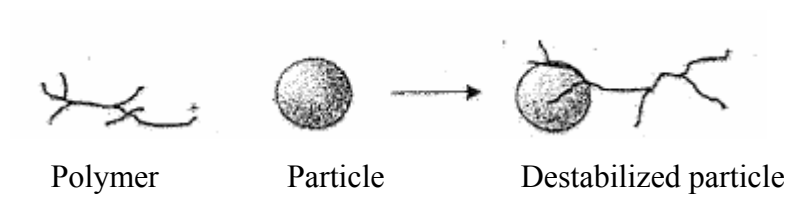
Reaction 2. The tail of the adsorbed polymer extends out into the bulk solution and becomes attached to vacant sites on the surfaces of another particle. This bridging leads to floc formation.

Destabilized particles   Floc
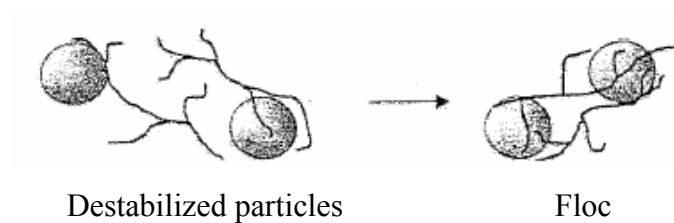
Reaction 3. If the extended segment fails to contact another particle it may fold back and attach to other side on the original surface-thus restabilizing the particle.

Destabilized particle   Restabilized particle
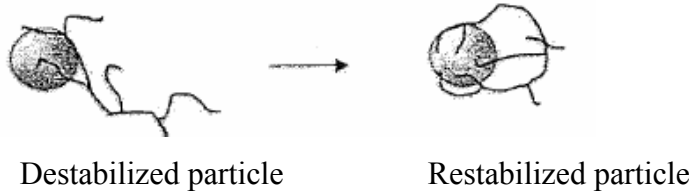
Reaction 4. If the excess polymer is added, the segment may saturate the surface of colloidal particle so that no sites are available for the formation of polymer bridges. This can restabilize the particles and may or may not be accomplished with charge reversal.

Excess polymer   Particle   Restabilized particle
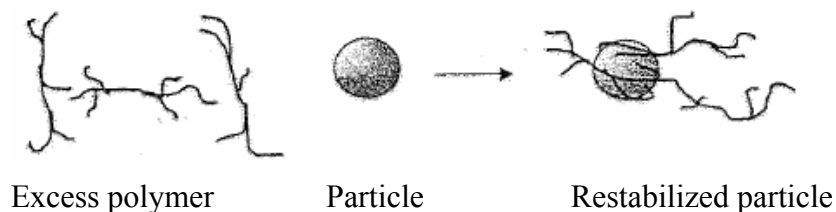
Reaction 5 : Rupture of particles if mixing is too high.

Floc   rupture of flocs
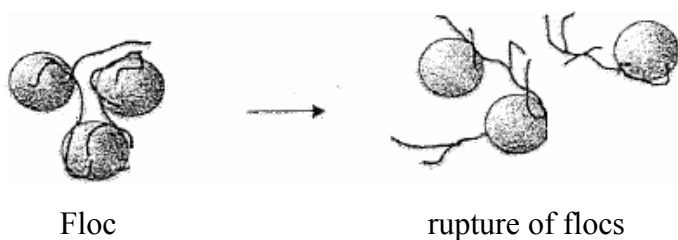
2.1.4.2. Charge Neutralization. Charge neutralization has been considered as one of the most important aspects in chemical conditioning. Charge is neutralized by the addition of coagulants giving rise to oppositely charged ions carried by the particles, for example inorganic salts such as NaCl, CaCl$_2$, Al$_2$(SO$_4$)$_3$ which give rise to Na$^+$, Ca^{+2} and Al^{+3}. The highly charged cations are very effective. Al^{+3} and Fe^{+3} salts are mainly used. Inorganic coagulants (such as alum) and cationic polymers often work through charge neutralization to form stable flocs. The sludge particles are negatively charged. This charge causes adjacent particles to repel each other and prevents effective agglomeration and

flocculation. As a result, charged colloids tend to remain discrete, dispersed, and in suspension. On the other hand, if the charge is significantly reduced or eliminated, then the colloids will gather together by forming first small groups, then larger aggregates and finally into visible floc particles which settle rapidly and filter easily. Neutralization is the key to optimizing treatment before sedimentation, granular media filtration or air flotation. Charge neutralization will not produce dramatic macroflocs alone. This is demonstrated by charge neutralizing with cationic polymer in the 50000-20000 molecular weight range.

Charge neutralization arises when the amount of polymer required to cause efficient flocculation corresponds with that required to give net zero electrophoretic mobility. The molecular weight and ionic strength effects have not been explained by a charge neutralization mechanism. The illustration of the charge neutralization mechanism is given in Figure 2.8. This has resulted in the development of the "electrostatic patch model". This model applies when the particles have a fairly low density of immobile surface charges and the adsorbing polymer has a high charge density. The particles may have "patches" of adsorbed polymer and these patches are able to contact with bare, but oppositely charge, surfaces on another particle giving quite strong attachment (Glover et al., 2001). The illustration of the patch mechanism is given in Figure 2.9.
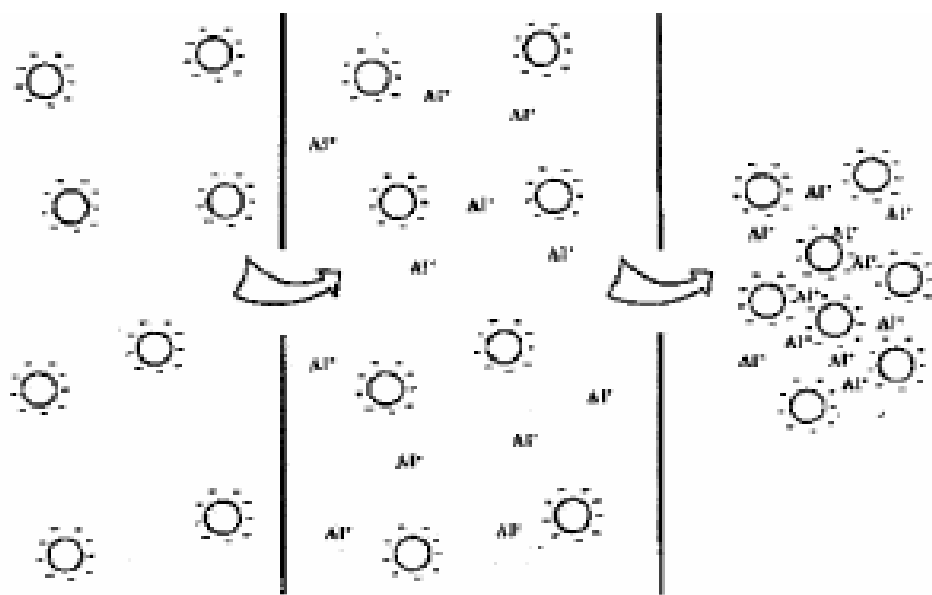
Figure 2.8. Charge neutralization mechanism

Charge neutralization is easily monitored and controlled using zeta potential. This is important because overdosing can reverse the charge on the colloid, and redisperse it as a positive colloid resulting in poor flocculated system. The detrimental effect of overdoing is especially noticeable with very low molecular weight cationic polymers that are ineffective at bridging.
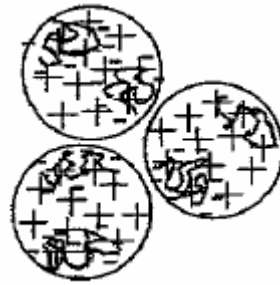
Figure 2.9. Patch mechanism (Glover et al., 2001)

The stability of a colloidal suspension depends on the balance between the forces attraction and repulsion (Water Treatment Handbook, 1991) given in Figure 2.10. Curve A shows the attraction forces, curve R shows the repulsion forces and curve S is the summation of curves A and R and is the actual potential curve followed by two particles approaching each other.

Particles are subjected to two major forces:

- Van der Walls force is the attractive force between two particles. This attraction between two particles is actually the results of the forces between individual molecules in each particle. An attractive energy curve is used to indicate the variation in attractive force with distance between particles. This attraction is very short-ranged, particles must be closer each other before it dominates. Van der Waals force is shown as a negative curve.
- Electrostatic repulsive force becomes significant when two particles approach each other and their electrical double layers begin to overlap. The level of energy required increases dramatically as the particles are closer. The maximum height of the curve is related to the surface potential. Electrostatic repulsion is always shown as positive curve.
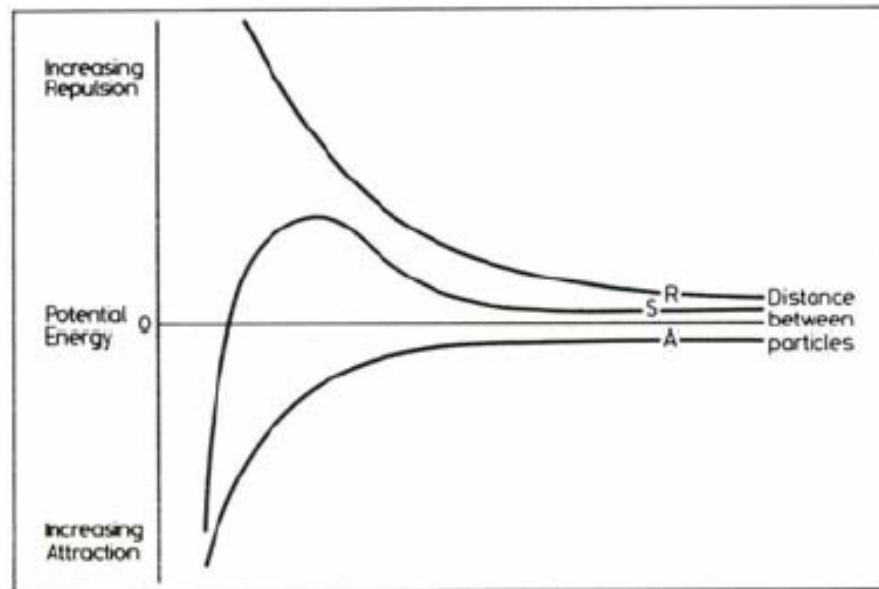
Figure 2.10. Repulsive and attractive forces (Moss and Dymond, 2006)

2.1.4.3. Double Layer. The electrical double layer is the combined system of the surface charge on the particle and the corresponding counterion charge in solution. Each particle carries a charge at its surface is exactly balanced by an equivalent number of oppositely charged counterions in solution by electrostatic interaction. The surface charge of the particles in wastewater is usually negative. Initially, attraction from the negative particle causes some of the counterions to form a firmly attached layer around the surface of the particle. This layer of counterions is known as the bound layer. Additional counterions are attracted by the negative particle; however, they are repelled by the positive bound layer as well as by other nearby positive ions. A dynamic equilibrium results, a diffuse layer of counterions formed, extending from the bound layer out into the bulk solution. The diffuse positive ion layer has a high concentration near the particle which gradually decreases with distance until it reaches equilibrium with the normal counterion concentration in solution. At any distance from the particle surface, its charge density is equal to the difference in concentration of positive and negative ions at that point. Charge density is the greatest near to particle and rapidly diminishes towards zero as the concentration of positive and negative ions merge together. The attached counterions in the bound layer and the charge atmosphere in the diffuse layer as called as double layer. The electrical potential is the highest at the particle surface and reduced with distance, approaching zero at the outside of the diffuse layer. The potential curve indicates the strength of the repulsive force between

particles and the distance. The potential at the junction of the bound layer and the diffuse layer is known as the zeta potential. Zeta potential is very effective tool for coagulation control because changes in zeta potential indicate changes in the repulsive force between particles (Moss and Dymond, 2006). The figure of double layer mechanism is given Figure 2.11.
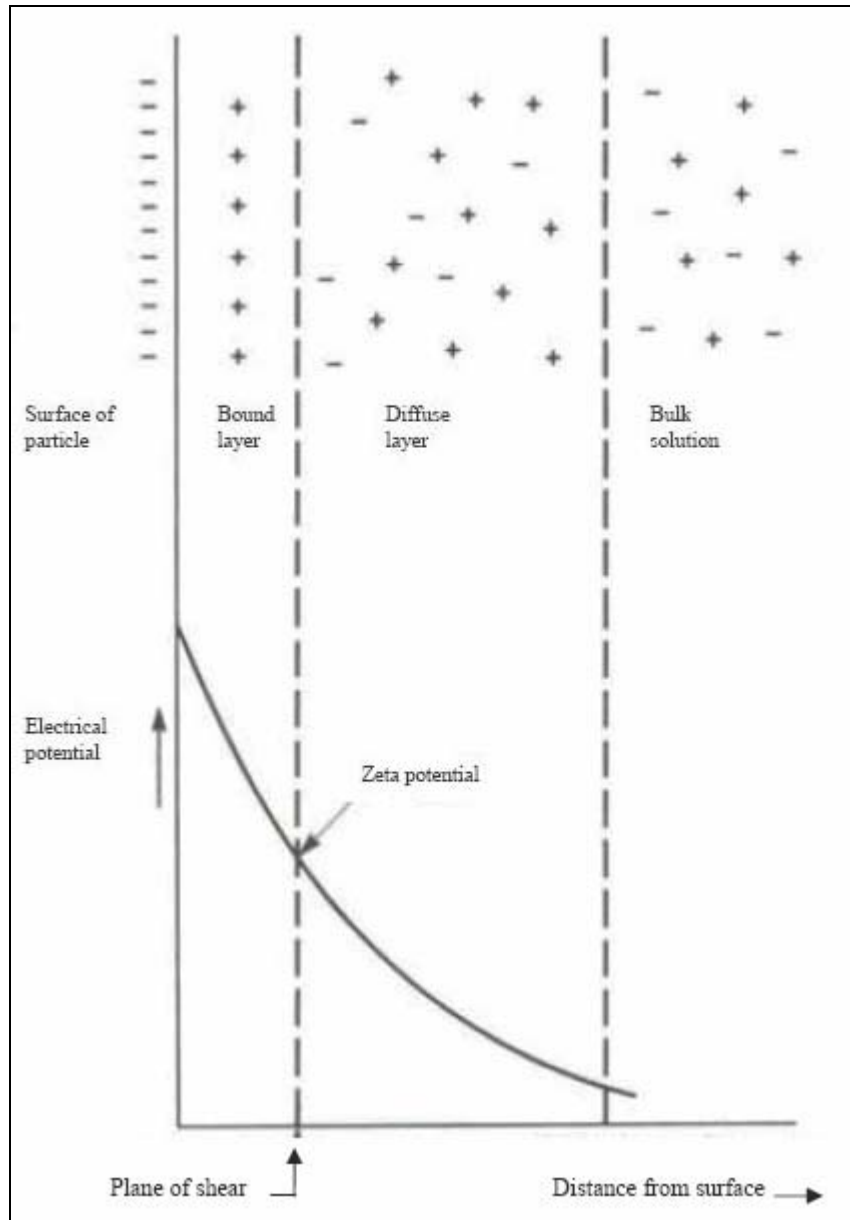
Figure 2.11. The double layer mechanism (Moss and Dymond, 2006)

2.1.4.4. Enmeshment (Sweep coagulation). Particles entrapment involves adding relatively excess doses of coagulants, usually aluminum or iron salts which precipitate as hydrous metal oxides. The amount of coagulant used is in excess of the amount needed to neutralize the charge on the particle surface. Some charge neutralization may occur, but most of particles are swept from the bulk of the water by becoming enmeshed in settling hydrous oxide flocs. This mechanism is often called enmeshment (sweep floc) (Ravina and Moramarco, 1993).

2.2. Dual Conditioning

The sludge dewatering has been known as one of the most expensive and hard to handle process in water and wastewater treatment. Safe and economic disposal of sludge can be achieved by reducing the volume of sludge. Conditioning improves the dewaterability characteristics of sludges by enhancing the flocculation. Polymers are commonly used for sludge conditioning to improve sludge dewaterability. Conventionally, a single polyelectrolyte is used in sludge conditioning by involving charge neutralization and particle bridging. In recent years, there have been several studies on dual polyelectrolyte systems to improve the flocculation of particles in water and wastewater treatment processes.

Chitikela and Dentel (1998) studied that when sludge conditioned with polymers, less amount of solid cake achieved due to the lower dosage requirement of polymer compared to the addition of fly and inorganic chemicals. According to their data, use of polymers in dual conditioning reduced the sludge dewatering and disposal cost to almost half. They also found that better dewaterability was achieved using same or less amount of polyelectrolytes than that of single conditioning.

Christensen et al. (1993) stated that good control of polyelectrolyte dose is critical in sludge conditioning, since overdosing will increase cost and reduce the sludge dewaterability. They also concluded that the optimal polyelectrolyte dosage is associated with the colloidal surface of minimum surface charge and a tendency to aggregate to form large floc. They also proposed that excess polyelectrolyte remains in the liquid part of

sludge, and the increase in the supernatant viscosity results in the deterioration of dewaterability.

Lee and Liu (2000) investigated the sludge conditioning by single and dual polyelctrolytes. They found that enhanced dewaterability could be achieved at identical polyelectrolyte dosage when sludge preconditioned with cationic polymer followed by nonionic polymer. It was proposed that when sludge was preconditioned with the cationic polymer, it is adsorbed on the sludge particles and primary flocs are formed. They are relatively more compact primary flocs due to the electrostatic attraction between cationic polymer and the negatively charge sludge particles. The subsequent addition of nonionic polymer then provided bridging of primary flocs into larger and stronger flocs by adsorbing on the loops and tails of the cationic polymer by hydrogen bonding and van der Waals force. The adsorption of mixed polymers on particle surfaces formed an extended conformation of polymers. The thicker and more expanded mixed adsorption layer contributed to the enhanced flocculation and enhanced dewaterability. Lee and Liu (2000) also proposed that better particle capture efficiency could be achieved in dual conditioning with a less chance of overdosing. Fine particle capture prevents the blinding of the filter and provides the nutrient release from sludges of biological nutrient removal plants. Lee and Liu (2000) proposed the mechanisms of sludge conditioned with dual polymers are illustrated in Figure 2.12. In Figure 2.12.a., the more compact primary flocs are formed when pre-conditioned with the cationic polymer, and the subsequent addition of the nonionic polymer then provides bridging of the primary flocs into aggregates. Figure 2.12.b. shows the illustrated mechanism of sludge pre-conditioned with the nonionic polymer followed by the subsequent addition of the cationic polymer.
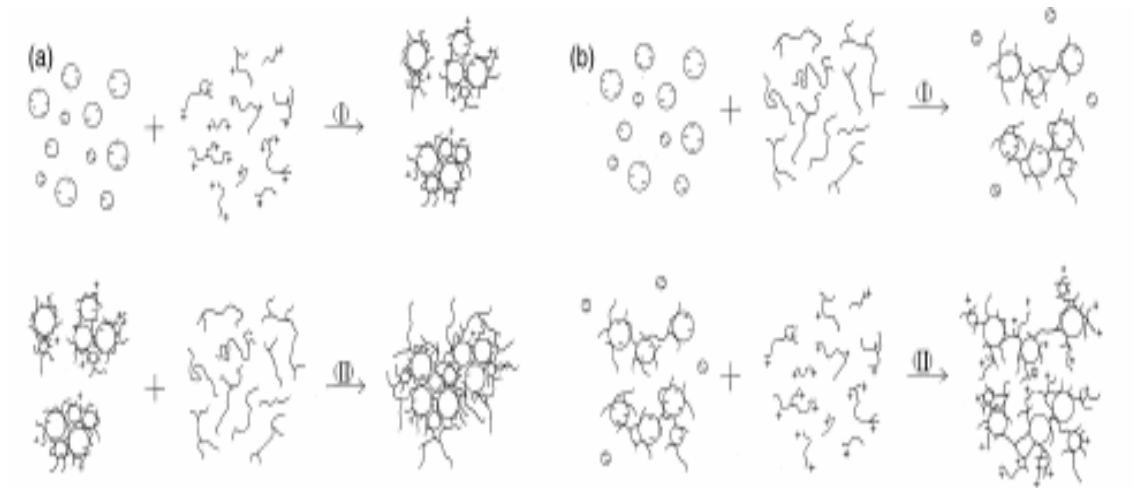
Figure 2.12. The mechanism of sludge conditioning by dual polymers (Lee and Liu, 2000)
(a) Sludge preconditioned with the cationic polymer followed by the nonionic polymer
(b) Sludge preconditioned with the nonionic polymer followed by the cationic polymer

Chen et al. (1996) indicated that the floc density and floc diameter are affecting the settling behaviors. However, the size of floc is relatively more significant in determining settling rate. Judging from the settling rate, sludge conditioned with dual polyelectrolytes should have larger flocs than sludge conditioned with a single polyelectrolyte. Lee and Liu (2000) indicated that sludge preconditioned with cationic polymer followed by nonionic polymer had the faster settling rate than sludge preconditioned with nonionic polymer followed by cationic polymer. They also noted that sludge preconditioned with the cationic polymer formed more compact aggregates than sludge preconditioned with the nonionic polymer, resulted in the lower ultimate sediment height.

Peng and Lu (1998) investigated that use of high molecular weight anionic polymer combined with a low molecular weight cationic polymer improved the settling rate and supernatant clarity. The sequence of addition of the two polymers was found to have a marked effect on the settling rate.

Wu et al. (1997) found that the increase in floc size caused the poor dewaterability of alum sludges in single conditioning while increasing bound water content. Moreover, decrease in floc density is caused by variations in both floc size and aggregation type.

Bache and Al-Ani (1989) showed that the larger flocs tended to be more fragile. In disagreement with Bache and Al-Ani (1989), Wen and Lee (1998) showed that, in clay particles flocculation, the floc strength increased with the floc size. Lee and Liu (2001) observed that when sludge was preconditioned with nonionic polymer, the relatively stronger primary flocs were formed. After adding the cationic polymer on nonionic polymer, obtained flocs showed a better floc strength than that of single polymer conditioning. The higher floc strengths prevents flocs from collapse during filtration. They also indicated that the sludges were dual conditioned with nonionic and cationic polymers, a better dewaterability was achieved with a less chance of overdosing regardless of the dosing sequence.

Yu and Somasundaran (1993) indicated that the combined use of a low molecular weight cationic polymer followed by a high molecular weight anionic polymer improved the flocculation. In agreement with Yu and Somasundaran (1993), Senthilnathan and Sigler (1993) found that the best dewaterability was achieved when the sludge preconditioned with low molecular weight cationic polymer followed by a high molecular anionic polymer.

Fan et al. (2000) investigated the effect of combinations of a polyacrylic acid (PAA) and a high molecular weight cationic copolymer of acrylamide and quaternary acrylate salt (Percol). They also investigated the effects of the molecular weights of PAA and Percol as well as charge density effect of Percol to understand the mechanism of dual conditioning. They proposed that flocculation of alumina sludges markedly enhanced by pre-conditioning with PAA, followed by Percol. First polymer added into the sludges was adsorbed on the alumina particles by electrostatic interaction and formed primary flocs. It was served as anchors for the adsorption of the second polymer. The schematic representation of the dual polymer flocculation process proposed by Fan et al. (2000) is given Figure 2.13. When larger PAA was added into the sludges, larger primary flocs formed while decreasing the requirement of the optimum dosage of the second polymer. Additionally, a wider molecular weight distribution of PAA widen the optimum dosage range of the second polymer. They also studied the sequential and co-addition conditioning. The better sludge dewaterability was achieved with the sequential addition of dual polymers.
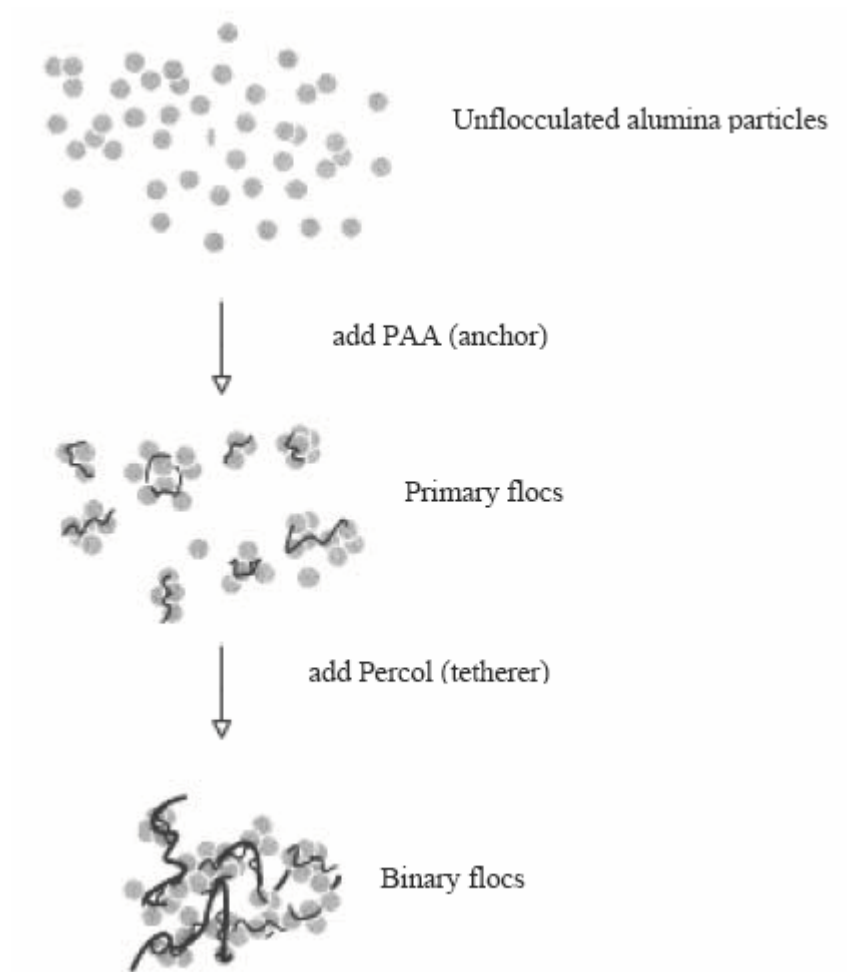
Figure 2.13. The schematic representation of the dual polymer flocculation process (Fan et al., 2000)

Glover et al. (2004) investigated the effect of dual polymer flocculation on the compressive yield stress and hindered settling function of positively charge alumina suspensions as measured by a pressure filtration technique. The primary aggregates were formed using low molecular weight polyacrylic acid (PAA) under two different shear mixing conditions at pH 5. This resulted in two types of aggregates with different mass fractal dimension and size. These aggregates were conditioned using either high molecular weight cationic or anionic long-chain polymer at the same pH. The aggregates obtained from dual conditioning resulted in increase the solid cake. The lower yield stress was found in the dual conditioning with high molecular weight polymer than that of single conditioning. In dual conditioning, the lower final cake moisture (28 per cent w/v) was achieved while maintaining a reasonably rapid filtration rate than that of single

conditioning (34.7 per cent w/v). Additionally, the polymer dosage required to achieve the good supernatant clarity was decreased from that of the single conditioning when dual polymer conditioning polymers were used.

Senthilnathan and Sigler (1993) indicated that dual cationic polyelectrolytes conditioning with the combination of high and low molecular weight is more effective than single polyelectrolyte conditioning. This dual conditioning enhanced solid capture and the reduced blinding of the belt filter media. They found that dual conditioning improved the dewaterability of sludge while increasing the solid content of sludge cake by 20 to 30 per cent. The solid content of sludge cake was increased from 8-11 per cent range to 11-14 per cent range in dual conditioning. The sludge cake was found to be much stronger in dual conditioning than that of single conditioning. The stronger sludge cake resulted in more pressure applied on the sludge cake without causing extrusion through filter media.

Most of the studies have investigated a combination of cationic and anionic polymers with the exception of some researchers. Swerin et al. (1997) investigated that the adsorption and flocculation caused by two cationic polymers. Böhm and Kulicke (1997) observed that better dewaterability of dredged sediment was achieved when conditioned with both cationic and anionic polymers simultaneously, although similar were not found when applied to sewage sludge.

Pinotti and Zaritzky (2001) investigated the performance of aluminium sulphate in comparison to two different polyelectrolytes (chitosan and polyacrylamide) as conditioning chemicals for the treatment of food processing wastewater. The obtained results indicated that the time necessary to produce system clarification was larger for aluminium sulphate than for polyelectrolytes. However, the lowest turbidity was achieved by the use of aluminium sulphate and chitosan.

2.3. The Rheological Characterization of Sludges

Rheological characteristics of sludge have been successfully used for the improvement of sludge treatment processes. A successful polymer dosage optimization and control system can offer significant financial benefits. In recent years, sludge rheology based parameters are used in the developed systems for polymer dose control.

Rheology describes the deformation (strain) of a body under the influence of stress (Abu-Orf and Dentel, 1999). In Newtonian fluids and suspensions, the shear stress is linearly related to the shear rate, according to the equation 2.1.

$$\tau = -\mu \, (dv/dy) \tag{2.1}$$

where τ represents the shear stress (Pa), dv/dy represents the velocity gradient or shear rate (1/s), and μ represents viscosity (cps). The negative sign is frequently omitted for convenience.

In Newtonian liquids, the viscosity in the equation 2.1. is considered constant for a specific temperature and solids concentration in the suspension. At a constant temperature, variations in the polymer and solid content can considerably alter the suspension viscosity according to the equation 2.2.

$$\eta = \eta_0 \, (1 + 2.5\varphi) \tag{2.2}$$

where η, η_0 are the viscosity of suspension and solvent respectively (cps). φ represents the volume fraction of suspension occupied by particles and/or polymer.

This equation is a key relationship between a sludge viscosity and its dewaterability. An increase in φ and η accomplished not only by increase in concentration of solids, but also by the incorporation of water into particle structure. Both the biosolids in wastewater sludges, and the polymer used in their conditioning are capable of incorporating and orienting substantial amounts of water. This may have significant effects on sludge,

centrate or filtrate viscosity. In addition, residual polymer resulting from overdosing will increase the solvent viscosity (Dentel, 1997).

Newtonian relationship is not valid for sludges. Wastewater sludges are non-Newtonian fluids, because the shear rate or the velocity gradient is not linearly proportional to the shear stress. However, the sludge viscosity is typically a function of shear rate. Rheological behavior describing the non-Newtonian behavior include the Ostwald equation, the Herschel-Bulkley equation and the Bingham equation as shown in equation 2.3, 2.4 and 2.5 respectively.

$$\tau = \eta_p \, (dv/dy)^n \tag{2.3}$$

$$\tau = \tau_0 + \eta_p \, (dv/dy) \tag{2.4}$$

$$\tau = \tau_0 + \eta_p \, (dv/dy)^n \tag{2.5}$$

where τ_0 = yield stress (Pa), η_p = plastic viscosity (cps) and n = empirical constant less than one.

The presence of the initial yield stress in the Bingham plastic and Herchel-Bulkley models is due to the resistance of the sludge solids to deformation until sufficient stress is applied to exceed the yield strength of the solid phase. The shear rate is generally not determined directly, but related to a velocity. The shear stress is related to a pressure, force or torque.

The use of rheological measurements is very useful in understanding wastewater treatment performance, since these measurements describe the flow and deformation properties of solid-liquid suspension from a fundamental perspective. Most researchers investigated the relationship between the sludge rheological parameters and other sludge properties such as total solids, capillary suction time (CST). Dick and Buck (1985) showed that the yield strength of the sludge varied exponentially with the suspended solids (SS). Christensen et al. (1993) observed a critical solids concentration in order to exhibit an

initial yield stress. Campbell and Crescuolo (1989) observed that the yield strength of the conditioned sludge increased with polymer addition up to the optimum dose.

Campbell and Crescuolo (1982) suggested that the derivative of the torque or shear stress vs. shear rate curve, termed the instantaneous viscosity, could be used as a control parameter. When the initial peak becomes apparent at a proper polymer dose, a zero derivative would be detected. As increasing polymer dosages improve the dewaterability, the CST decrease and height of the rheogram peak increases.

Dentel and Abu-Orf (1995) suggested that decrease in viscosity could be attributed to decreases in the concentration of fine particles in the supernatant, additionally increase in viscosity were attributed to excess polymer or the saturation adsorption of polymer.

Ayol et al. (2006) investigated the rheological behaviors of thermophilic-mesophlic anaerobically and mesophilic aerobically digested biosolids evaluating the peak stress value and the network strength energy. They found that sludges exhibited non-Newtonian and greater shear rates led to a decrease in shear strength, probably due to the disruption of the conditioned sludges.

3. MATERIALS AND METHODS

3.1. Characteristics of Materials Used

3.1.1. Sludge Characteristics

In this study, the alum sludge was provided from Kağıthane Water Treatment Plant located in Istanbul. It treats approximately 270000 m^3 of water daily. Alum was added to the secondary primary tank to improve the settability of sludge. The turbidity of the treated water is 0.1-0.3 NTU.

The sludge sample is taken from the bottom sludge of the clarifier and the filter wash water. The characteristics of alum sludge are tabulated in Table 3.1. All sludge samples were analyzed within 4 days after the sampling. They were stored at 5°C in the cold room until analysis. They were taken out of cold room to ambient temperature.

Table 3.1. Properties of the alum sludge used in the study

Parameters	Value
Total solids, %	0.7-1.5
Total solids, mg/L	5600-12000
pH	6.5-7.0
Zeta Potential[1], mV	-11.5 / -13.0
$AlSO_4$ Dosage[1], g/m^3	50
Conditioner Dosage[1], g/m^3	0.2
CST of Original Alum Sludge, s	150-185

[1] Data is taken from Kağıthane Water Treatment Plant

Total sludge solids were determined by a standard evaporation method. 50 mL of well-mixed sludge sample was evaporated in a preweighed dish in an oven at 103°C for 24 hours. The evaporation dish was taken out of an oven and cooled in a desiccator. The difference between the weight of dish and dish plus sludge sample represents the total sludge solids (APHA, 1975)

The pH values of the sludge were measured by WTW pH Meter Model 320 after calibration with pH 4, pH 7 and pH 10 (APHA, 1975).

3.1.2. Polymer Characteristics

Alum sludge has been recognised as difficult to dewater. It is often conditioned with polymer prior to dewatering (Zhao, 2004). The one major area of application of polymers is in the dewatering of sludges from clarifiers and filter backwash waters (CIBA, 2006).

Different types of polymers were used to determine the effects of single and dual conditioning on dewaterability of alum sludge. The polymers are in granular powder and micro-bead form obtained from CIBA Specialty Chemical Ltd., Water and Paper Treatment Segment. The appearance, molecular weight, charge density, bulk density, particle size, pH of 1% solution and viscosity at shear rate 5.11 s^{-1} of each polymer are given in Table 3.2.

Although polymer in granular form can be stored up to two years under cool and dry storage conditions, polymer solutions at 0.01-2 per cent can retain their efficiency for 1-2 days. After this period of time, there may be some loss of effectiveness depending on the storage conditions. All solutions should be kept in the dark condition when they are not in use. In this study, polymer solutions were kept for one day. The dose levels will vary considerably depending on water source for sludge thickening and dewatering. Sludges from turbid sources or lime softening processes can be dewatered easily. Sludges from low turbid, thin waters can be much more difficult to treat (CIBA, 2006).

Table 3.2. The physical properties of the polymers used in the study

Polymers	Appearance	Ionic Character	Molecular Weight	Charge Density, %	Bulk density, g/cm^3	pH of 1% solution	Particle size, μm	Viscosity of 1% solution at shear rate 5.11 s^{-1}, cps
Magnafloc 351	White granular powder	Nonionic	Low	-	0.80	3.5	< 1000 (98%)	500
Magnafloc 333	White granular powder	Nonionic	High	-	0.75	3.5	< 850 (98%)	900
Zetag 7632	White powder	Cationic	High	40	0.70	3.5	< 1400 (98%)	2100
Zetag 7563	White Micro-beads	Cationic	Low	40	0.80	3.5	< 1400 (100%)	1800
Zetag 7631	White powder	Cationic	High	80	0.70	3.4	< 1400 (98%)	2200
Zetag 7587	White Micro-beads	Cationic	Low	80	0.80	3.5	< 1000 (100%)	2000
Zetag 7623	White powder	Cationic	High	10	0.70	3.8	-	700
Zetag 7634	White granular powder	Cationic	High	15	0.70	3.8	-	1600
Magnafloc 525	White Micro-beads	Anionic	Low	70	0.80	6.5	< 425 (85%)	2000
Magnafloc 342	White granular powder	Anionic	High	15	0.75	7.0	< 1000 (98%)	2800
Magnafloc LT 25	White granular powder	Anionic	High	15	0.75	7.0	< 1000 (98%)	2800
Magnafloc 3105	White granular powder	Anionic	Low	15	0.85	6.5	< 1000 (98%)	1200
Magnafloc 2025	White granular powder	Anionic	Low	15	0.80	6.5	< 850 (98%)	1900

3.2. Experimental Procedure

3.2.1. Preparation of Polymer Solutions

Correct solution preparation of polymer is an essential prerequisite for laboratory evaluations. Polymer solutions were prepared according to methods proposed by the polymer manufacturer. In this study, polymer solutions were prepared at a 0.1 per cent on the basis of weight/volume (w/v) concentration by using nanopure water. The polymer dosages applied to the sludge samples were in the range of 0-5 mg/g dry solid (0-60 mg/L). In this study, polymer solutions were kept for one day.

3.2.2. Sludge Conditioning Process by using Jar Test

The jar test is a critical laboratory procedure used to determine the optimum operating conditions for water and wastewater treatment. This method allows adjustment in pH, variations in coagulant and polymers dose, alternating mixing speeds, or testing of different coagulant or polymer types on a laboratory scale in order to predict the functioning of a large scale treatment operation. This procedure also allows individual polymers to be compared on such criteria as floc formation, settling characteristic and clarity. Generally, the best performing products provide fast floc formation, rapid settling rate and clear supernatant. Jar testing is an experimental method where optimal conditions are determined empirically rather than theoretically. The values that are obtained through the experiment are correlated and adjusted in order to account for the actual determination.

The experiments were conducted by using Velp Scientifica Model F.6/S jar test apparatus that has the mixing speed range of 0 to 200 rpm. It has six mixing paddles with the width of 7.5 cm and the height of 2 cm. Every paddle was lifted 1.5 cm from the bottom of each beaker. The jar test apparatus is shown in Figure 3.1.

Single conditioning experiments were performed with polymer dosage in the range 0-5 mg/g dry solid to be added to 500 mL sludge samples. In each run, a number of 500 mL sludge samples poured into 1-liters beakers, and mixed with fixed dosage. Following polymer addition, sludge was subjected to 200 rpm for 120 s of rapid mixing followed by slow mixing at 30 rpm for 300 s to promote flocculation (Ayol et al., 2006). The conditioned samples were then utilized for further analyses.

In dual conditioning, the concentration ratio of the two polymers was adjusted to 1:1. Following first polymer addition, sludge sample was mixed at 200 rpm for 120 s of rapid mixing. After the sequential addition of second polymer, conditioning experiments were continued by remixing the samples at 200 rpm for 120 s of rapid mixing followed by slow mixing at 30 rpm for 300 s to promote flocculation.

3.2.3. Determination of Sludge Dewaterability by Capillary Suction Time (CST) Test

CST is a measure of sludge filterability as described by Vesilind (1988) that is expressed in seconds. High CST values indicate the slow releasing of the liquid part of sludges and low CST values show the easy separation of sludge water. Capillary suction time is used as an indicator of sludge dewaterability.

In this study, the test was performed with the CST apparatus supplied by Venture Innovations Inc. Figure 3.2. shows the CST Instrument (Venture Innovations, Inc.) in detailed.

Figure 3.1. Jar test apparatus used in the experiments

This CST device consists of two plastic blocks, a stainless steel collar, three electrical sensors fixed on the upper plastic block, and an electrical timer (Vesilind, 1988). Standard CST papers (Whatman No 17 filter paper) were used in the CST test to overcome the effects of filter paper. The filter paper is placed between these two blocks. Two milliliters of sludge samples is poured into the stainless steel collar. The radius of inner cylinder of the collar is 0.95 cm. The diameters of first circle on the upper plastic block, which had two sensors on it, second circle on which one sensor is present, are 3.2 cm and 4.6 cm respectively. When the sample is reached first two sensors, the electrical signal starts the timers. After a period, the sensor of outer circle is perceived the liquid part of the sludge sample, then, the timer is stopped. The period of reaching from the inner circle to the outer circle is called as "Capillary Suction Time (CST)" in seconds.

The CST test depends on the sludge solids concentration and the instrument used. Temperature also affects the test due to its effect on viscosity (Vesilind, 1988).

All measurements were performed at room temperature. The CST tests were triplicated to take the more reliable test results.

3.2.4. Turbidity

The supernatants of the conditioned samples were withdrawn for turbidity measurement after 15 minutes settlement. Turbidity tests were conducted by HACH 2100P Turbidimeter. The turbidimeter apparatus is shown in Figure 3.3.

Figure 3.2. Capillary suction time (CST) apparatus

3.2.5. Microscopic Analysis

The change in the floc structure after polymer conditioning was observed with the microscopic pictures of sludge samples. Krüss Optronic MLB 2100 model microscope was used with achromatic lenses with an x4 eyepiece. It has triconular head with binocular head angled at 45°C, equipped with two 10x flat-field eyepieces with inter-ocular distance adjustment and with a vertical optical connection for microphotography. The micrometer is 12 mm long and has 120 divisions. Microscope stage with vernier scale graduated in divisions of 0.1 mm. 6V 20W Tungsten-Halogen bulb with brightness adjustment is used for illumination.

The micrographs were transferred to the computer by the spot insight color cooled digital camera NIKON 4500 with PC archive and measurement software. The microscope equipment is shown in Figure 3.4.

3.2.6. Rheological Analysis

In this study, the rheology measurements of the conditioned sludge samples were performed by using HAAKE RheoStress1. The test set up and rheometer controlling were done by the use of the software program RheoWin Pro 2.91. This instrument is capable of measuring the shear stress at different controlled shear rates. All rheology measurements were obtained at a constant temperature of 25°C. The shear rate was increased from 0 to 100 s^{-1} in 60 s. This acceleration rate provided distinctive peaks in the produced rheograms for the conditioned sludge samples at the optimum dosage. Figure 3.5. shows the HAAKE RheoStress1 instrument used in this study.

Figure 3.3. HACH 2100P Turbidimeter used in the experiments

Figure 3.4. Krüss Optronic MLB 2100 microscope used in the experiments

Figure 3.5. HAAKE Rheostress1 instrument used in this study

4. RESULTS AND DISCUSSIONS

This study investigates the dewaterability of alum sludges by applying single and dual conditioning. Besides the dewaterability of alum sludges, the rheological characterization of conditioned sludge samples was investigated. The dewaterability of sludge was determined by measuring filterability in terms of capillary suction time. Turbidity was measured in term of NTU by using turbidimeter. The rheological characterization of conditioned sludge samples was determined by HAAKE RheoStress1. The optimum polymer dosage was accepted as the polymer concentration giving the minimum CST value.

In this study, experiments were performed mainly with alum sludge provided from Kağıthane Water Treatment Plant located in İstanbul. The polymers are in granular powder or micro-bead form obtained from CIBA Specialty Chemical Ltd., Water and Paper Treatment Segment.

Polymer solutions (variations of polyacrylamides) were prepared according to methods proposed by the polymer manufacturer. In this study, polymer solutions were prepared at a 0.1 per cent (w/v) concentration by using nanopure water supplied from Organik Kimya Production Unit.

The results of this study are expressed graphically by using a color and a figure coding given in Table 4.1. In dual conditioning, the data are expressed with the legend ◊ in the figures, the color of the figure shows the ionic and charge characteristic of the polymer added second to the sludge samples.

Table 4.1. A color and a figure coding system used in the study

Polymer type	Polymer	Molecular weight	Shape	Ionic charge, %	Shape Color
Nonionic	Magnafloc 333	high	▲	-	
	Magnafloc 351	low	■	-	
Cationic	Zetag 7632	high	▲	40	
	Zetag 7563	low	■	40	
	Zetag 7631	high	▲	80	
	Zetag 7587	low	■	80	
	Zetag 7623	high	▲	10	
	Zetag 7634	high	▲	15	
Anionic	Magnafloc 525	low	■	70	
	Magnafloc 342	high	▲	15	
	Magnafloc LT 25 *	high	▲	15	
	Magnafloc 3105	low	■	15	
	Magnafloc 2025	high	▲	25	

* Magnafloc LT 25 and Magnafloc 342 have the similar physical characteristics, in order to differ them, Magnafloc LT 25 was defined with red color instead green.

4.1. Single Conditioning

Single conditioning experiments were carried out with 13 different polymers under the same mixing conditions by using a jar test equipment. In each run, a number of 500 mL sludge samples poured into 1-liter beakers, dosed with desired amount of polymer. Following the polymer addition, the sludge samples were subjected to 200 rpm for 120 s of rapid mixing followed by slow mixing at 30 rpm for 300 s to promote the flocculation process. Then, capillary suction time (CST) of the conditioned sludge samples and turbidity of their supernatants were measured. The remaining conditioned sludge samples were kept for rheology analysis.

4.1.1. Single Conditioning with Nonionic Polymers

Magnafloc 333 and Magnafloc 351 are nonionic, high (HMW) and low (LMW) molecular weight polyacrylamides. The CST value of raw sludge was 185 s. The conditioning tests showed that the lowest CST values were measured in nonionic polymer dosages of 1.08 mg/g dry solid. The correspondingly, CST values at the same dosage of Magnafloc 333 and Magnafloc 351 were found to be 15.9 s and 19.8 s respectively. Further increase in the dosages of nonionic polymers slightly decreased in the sludge dewaterability. However, the optimal nonionic polymer dosage ranged from 1.08 to 2.31 mg/g dry solid.

Figure 4.1 illustrates the performance curve describing the relationship between high and low molecular weight nonionic polymer dosages (on dry basis) and the sludge dewaterability.

4.1.2. Single Conditioning with Cationic Polymers

Zetag 7632, Zetag 7563, Zetag 7631, Zetag 7587, Zetag 7623 and Zetag 7634 are cationic polyacrylamides. These cationic polymers vary in molecular weight and charge density. The physical properties of these polymers are given in previous chapter in Table 3.2. Figure 4.2 shows the relationship between the sludge dewaterability and the applied cationic polymer dosages.

In the cationic polymer conditioning tests, due to the time limitation, sludge samples were taken from same treatment plant in two different times (one week apart). This situation did not caused to an important change in the dewaterability characteristics of the sample. The CST of the sludge taken first was 172 s. The CST of the other sludge taken 1 week later was 187 s.
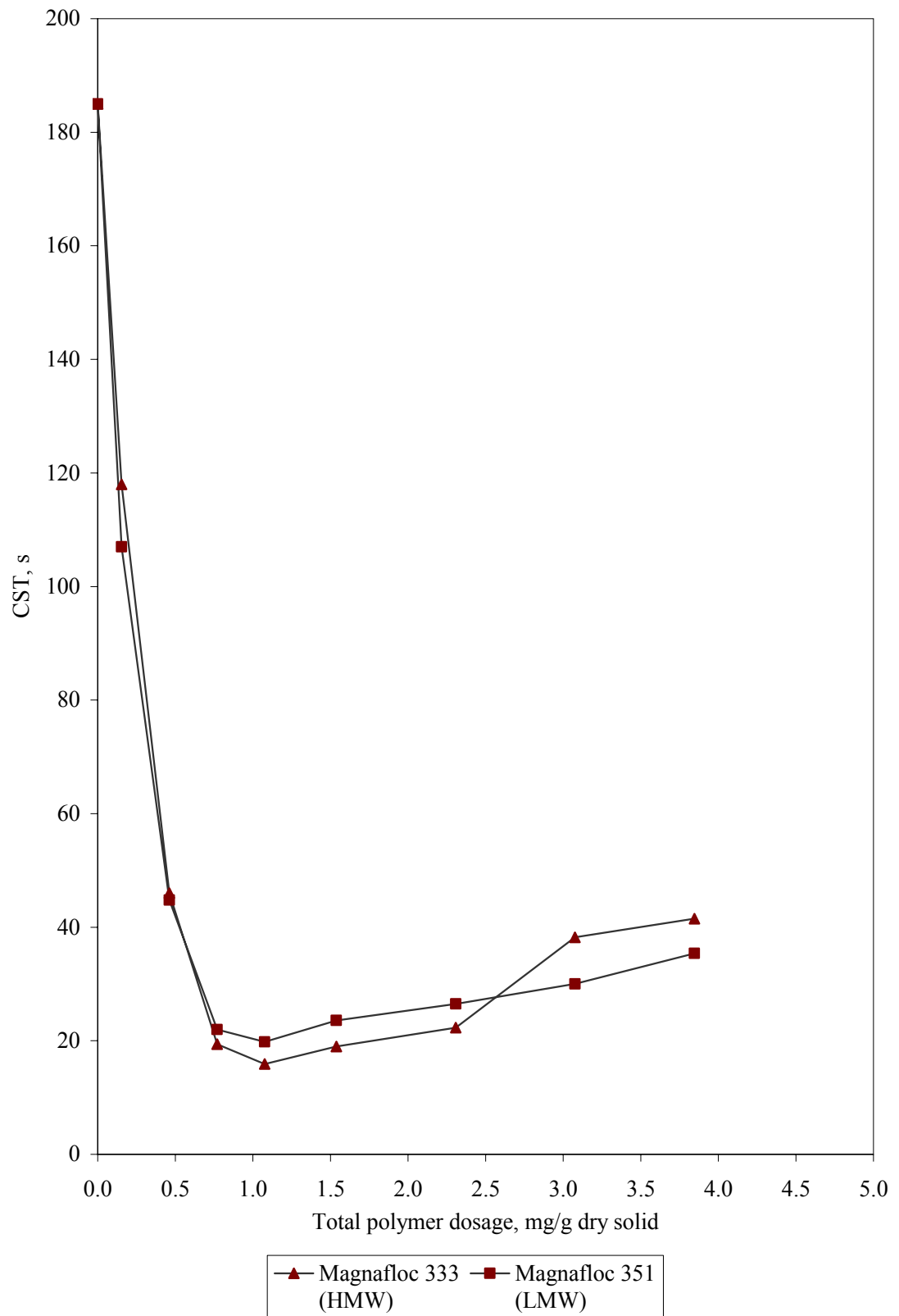
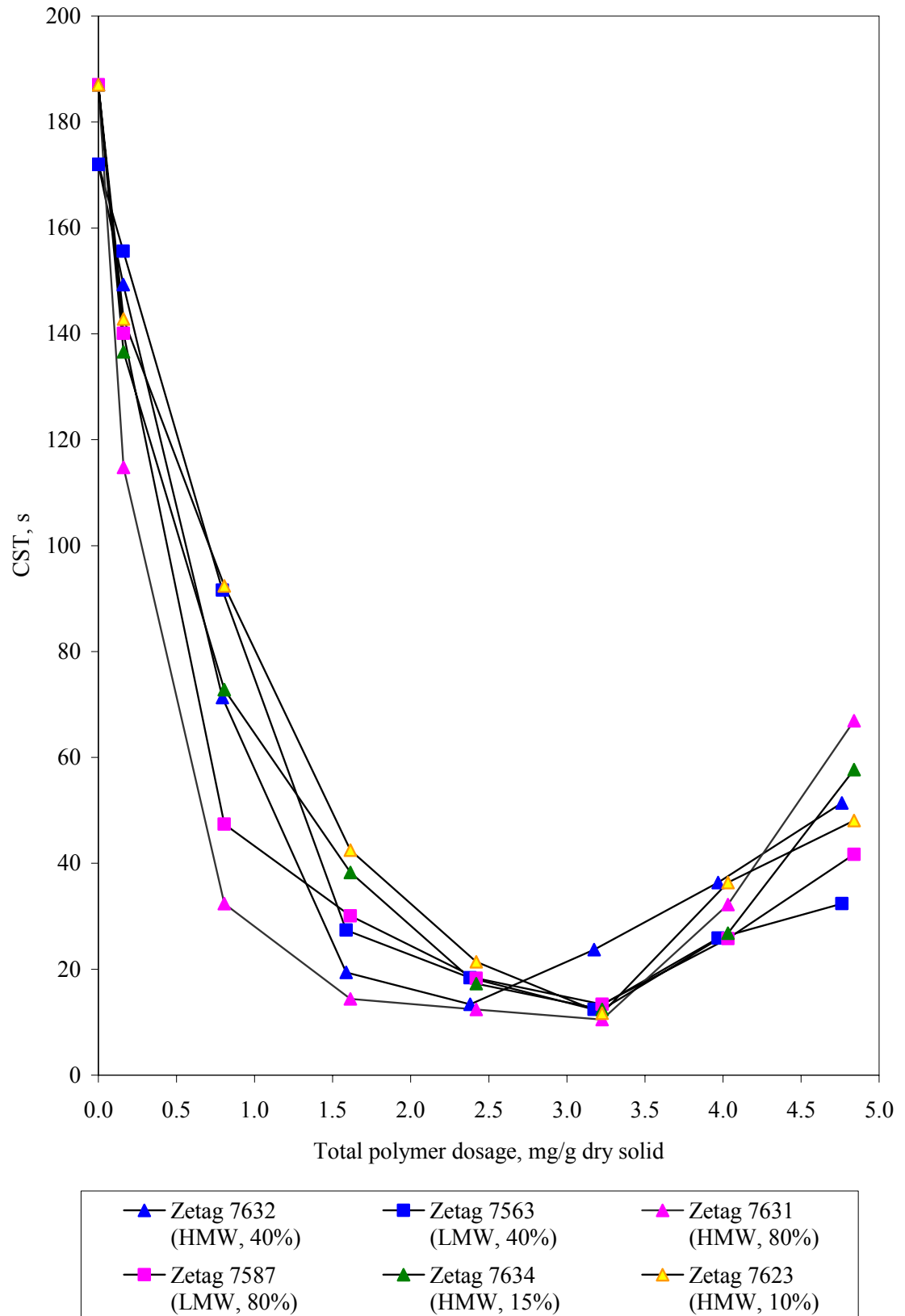Figure 4.1. Sludge dewaterability as a function of total nonionic polymer dosage for single conditioning.

Figure 4.2. The relationship between the sludge dewaterability and the dosage of cationic polymers.

The optimum dosage for Zetag 7631, Zetag 7587, Zetag 7634 and Zetag 7623 giving the minimum CST values was found to be 3.23 mg/g dry solid. The CST values of the samples conditioned with these polymers were 10.5 s, 13.4 s, 12.4 s and 11.7 s respectively. The optimum dosages for Zetag 7632 and Zetag 7563 were 2.37 s and 3.17 s respectively.

The CST values of the samples conditioned with these two polymers were 13.4 s and 12.4 s respectively. The lowest CST value was obtained as 10.5 s at the dosage of 3.23 mg/g dry solid in the single conditioning with Zetag 7631. Even with a lower dosage of 1.61 mg/g dry solid, Zetag 7631 gave lower CST values compared to the CST values of sludge samples conditioned with the optimum dosages of Zetag 7632 and Zetag 7563. The optimal polymer dosage for Zetag 7631 was then, accepted to be in the range of 1.61 to 3.23 mg/g dry solid.

4.1.3. Single Conditioning with Anionic Polymers

Like cationic polymer conditioning experiments, in the anionic polymer conditioning experiments, sludge samples were taken from same treatment plant in two different times. The CST values of raw sludge taken first and second were 154 s and 162 s respectively. This situation did not caused to an important change on the dewaterability characteristics of the sample sludges. The optimum polymer dosages for Magnafloc 525, Magnafloc 3105, Magnafloc 342 and Magnafloc 2025 were 2.5, 2.5, 0.76 and 1.52 mg/g dry solid respectively. The corresponding CST values of the conditioned sludge samples were 17.6 s, 12.5 s, 15.3 s and 24.3 s respectively. Figure 4.3 shows the relationship between the sludge dewaterability and the applied anoionic polymer dosages. Magnafloc 3105 and Magnafloc 342, having lower ionic charge of 15 per cent, provided the best dewaterability results compared to other two anionic polymers. This can be explained with that increasing negative charge density decreases the tendency to adsorb on negative particles, which limits flocculation process (Gregory, 1983).
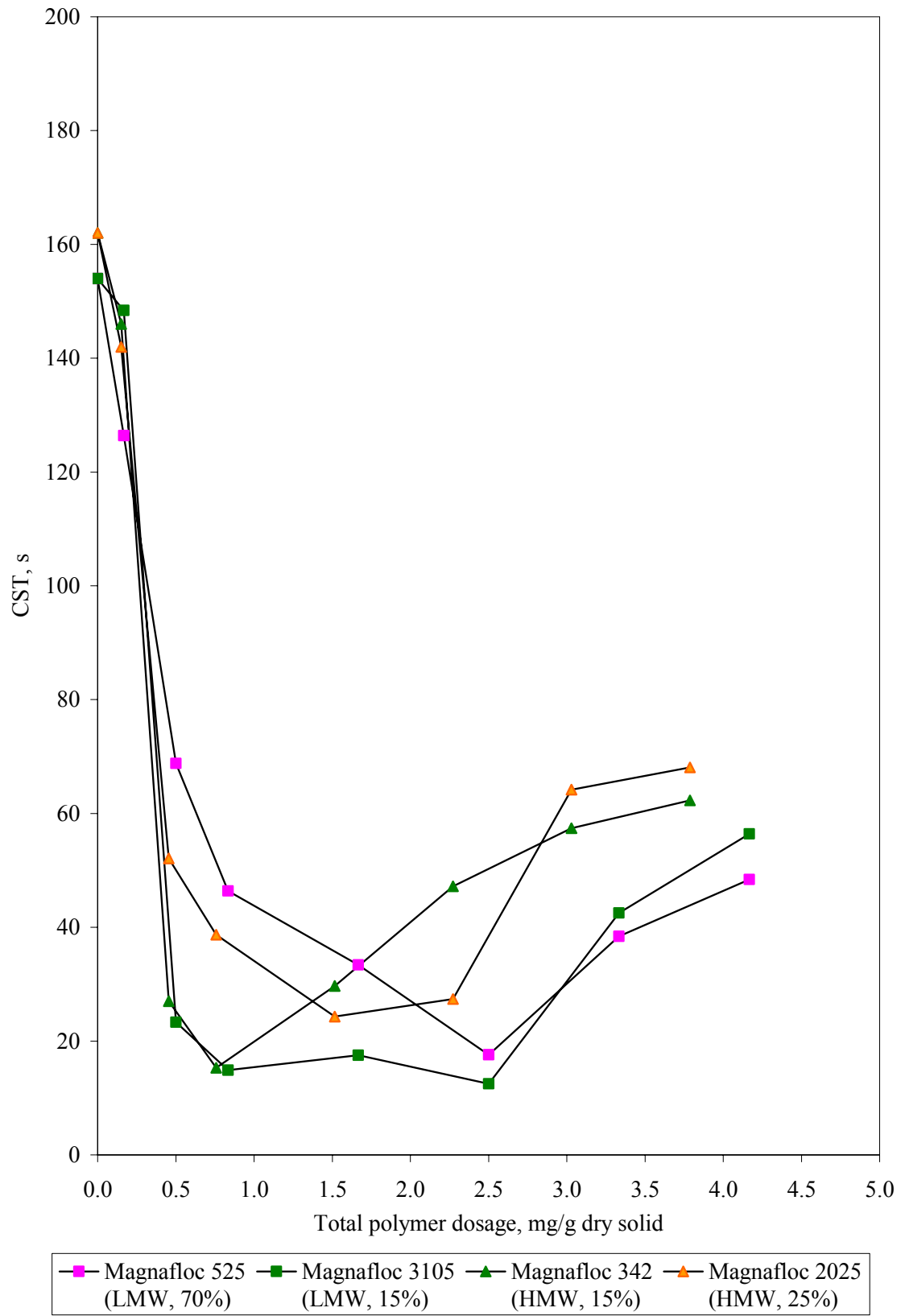
Figure 4.3. The relationship between the sludge dewaterability and the dosage of anionic polymers.

In the literature, sludge conditioning is generally performed with cationic and anionic polymer especially an anionic polymer of Magnafloc LT 25. The manufacturer recommend to use Magnafloc 525 instead of Magnafloc LT 25 for sludge treatment process. In this study, both of Magnafloc LT 25 and Magnafloc 525 were used for sludge conditioning. The conditioning test results showed that the performances of these two polymers were exactly the same. These two polymers have the same molecular weight and the charge density declared by the manufacturer. In polymer business, same product can be coded in different names depending on the different application areas. Based on our results, there is a possibility that Magnafloc LT 25 and Magnafloc 342 are same product with different names. Figure 4.4. illustrates performance curves of Magnafloc 342 and Magnafloc LT 25.

Based on our results, in the single conditioning, a better dewaterability was achieved by conditioning with the high and low molecular weight nonionic polymers. It is quite unusual to have a nonionic polymer outperform a cationic polymer. It is probably due to the relatively weak electrostatic attractive forces between the cationic polymer and the less negative charge of the sludge particles and the stronger bridging by nonionic polymer. Sludge samples conditioned with the optimum Magnafloc 333 dosage of 0.61 mg/g dry solid had the CST value of 20 s. On the other hand, the CST value of sludge sample conditioned with Zetag 7631 was found to be 10.5 s. It seems that cationic polymer improved the dewaterability of the sludge than nonionic polymer. However, nonionic polymer reached to a reasonable CST value at a much lower dosage compared to the cationic one. This might be an important cost benefit for the treatment plant. At the current time, the nonionic polymer Magnafloc 333 costs about 2.60 EUR/kg and the cationic polymer Zetag 7631 costs 3.20 EUR/kg. The full cost list of polymers used in this study is given in Table 4.2.

Table 4.2. The current cost list of polymers used in this study (September, 2006)

Polymers	Cost, EUR/kg
Magnafloc 351	2.65
Magnafloc 333	2.65
Zetag 7632	3.20
Zetag 7563	3.00
Zetag 7631	3.20
Zetag 7587	3.40
Zetag 7623	2.80
Zetag 7634	2.80
Magnafloc 525	3.40
Magnafloc 342	2.90
Magnafloc LT 25	2.90
Magnafloc 3105	2.40
Magnafloc 2025	2.40

Although, nonionic polymer gave the better dewaterability result in the single conditioning, the supernatant turbidity of the sludge samples conditioned with nonionic polymers was considerably higher than the cationic ones. The nonionic polymers were not effective in the fine particle capture as the cationic polymer. This makes it unusual to use the nonionic polymers for single sludge conditioning. The supernatant turbidity values of the single conditioned sludge samples are given in Figure 4.5., Figure 4.6. and Figure 4.7. Figure 4.8. shows that the supernatant turbidity curves for the best performing nonionic, cationic and anionic polymers in the single conditioning tests.

CST, s

Total polymer dosage, mg/g dry solid

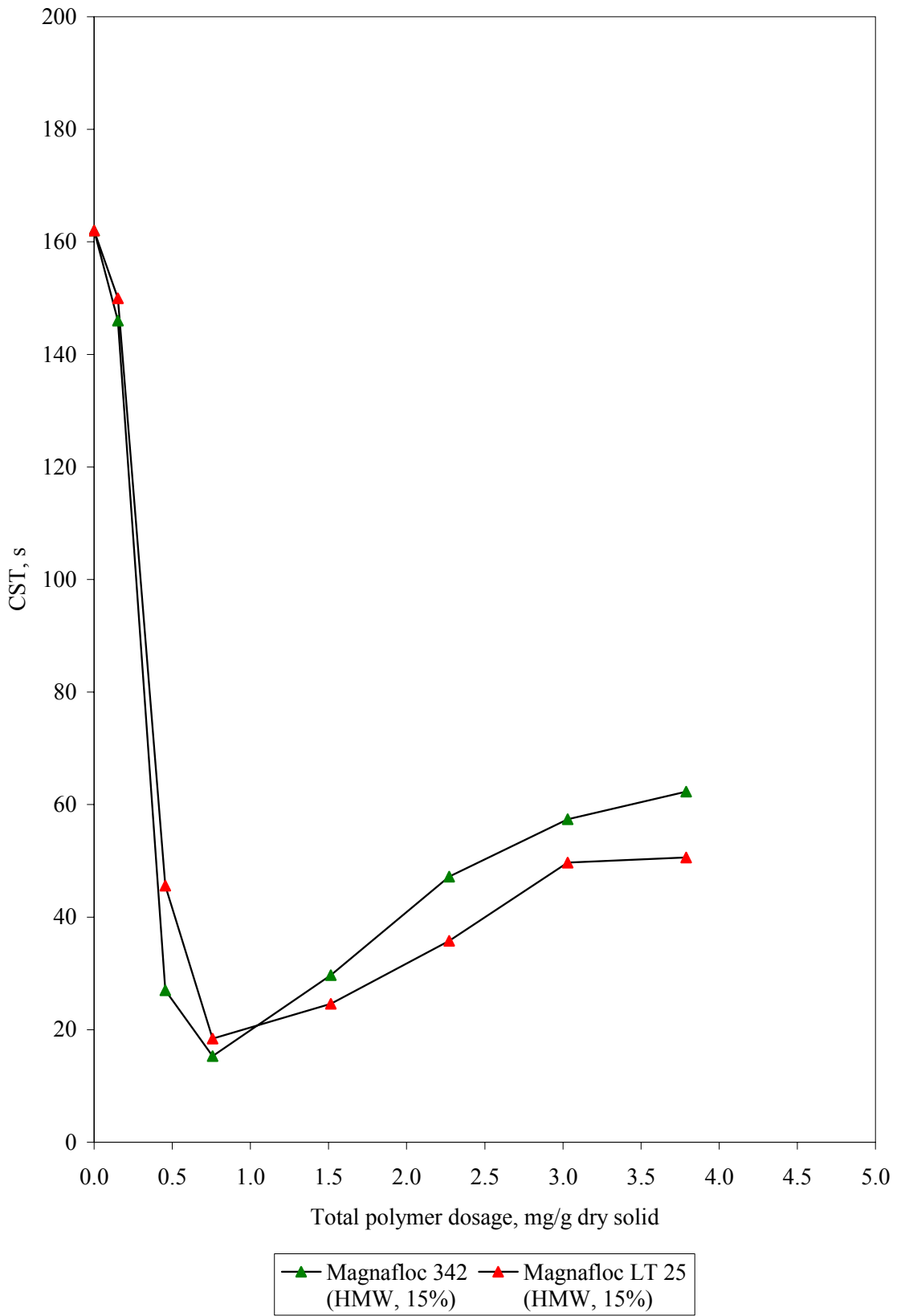Magnafloc 342 (HMW, 15%)   Magnafloc LT 25 (HMW, 15%)

Figure 4.4. Performance curves of anionic polymers Magnafloc 342 and Magnafloc LT 25 (anionic).

In single conditioning by nonionic polymers, the effective mechanism of flocculation is mostly the particle bridging instead charge neutralization. In this mechanism, it is difficult to capture the supracollodials into the floc structure. This can be explained the high turbidity in nonionic polymer conditioned sludge.

Glover et al. (2000) reported that the addition of the anionic polyacrylamide alone to the alumina at pH 7.5 results in some flocculation, which could be possible with hydrogen bonding mechanism. Since, both surface and polymer are negatively charged. The flocculation is poor, and the remaining supernatant is always turbid.
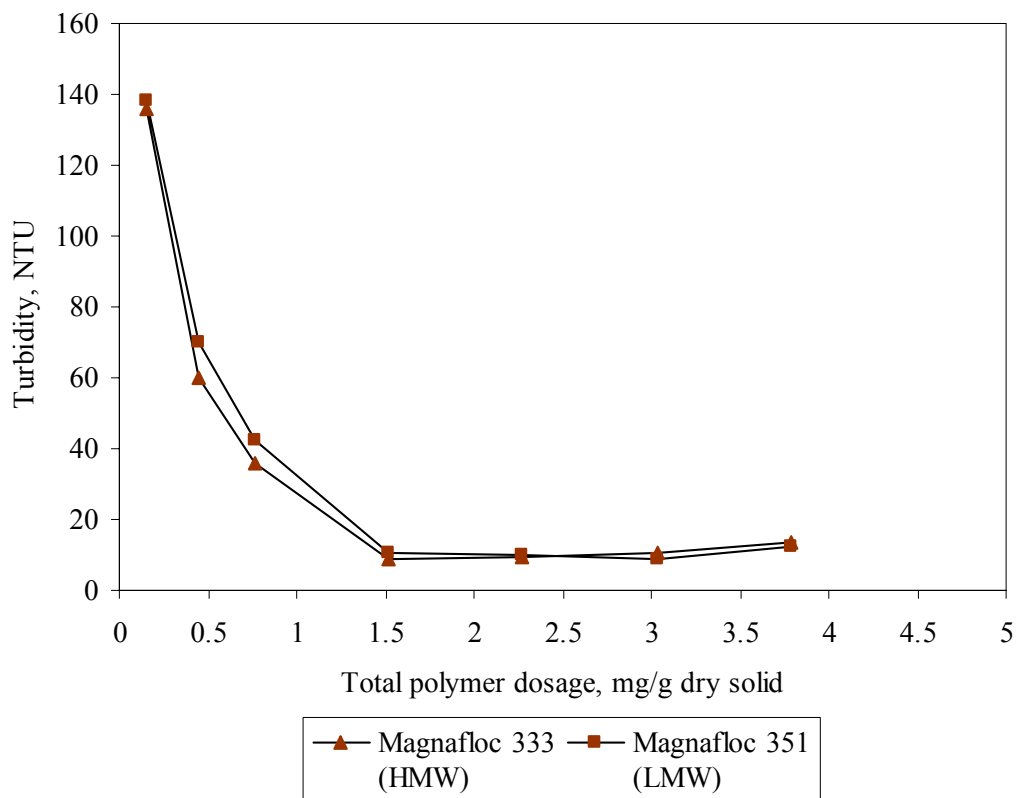

Figure 4.5. The supernatant turbidity of the sludge samples in the single conditioning with nonionic polymers.
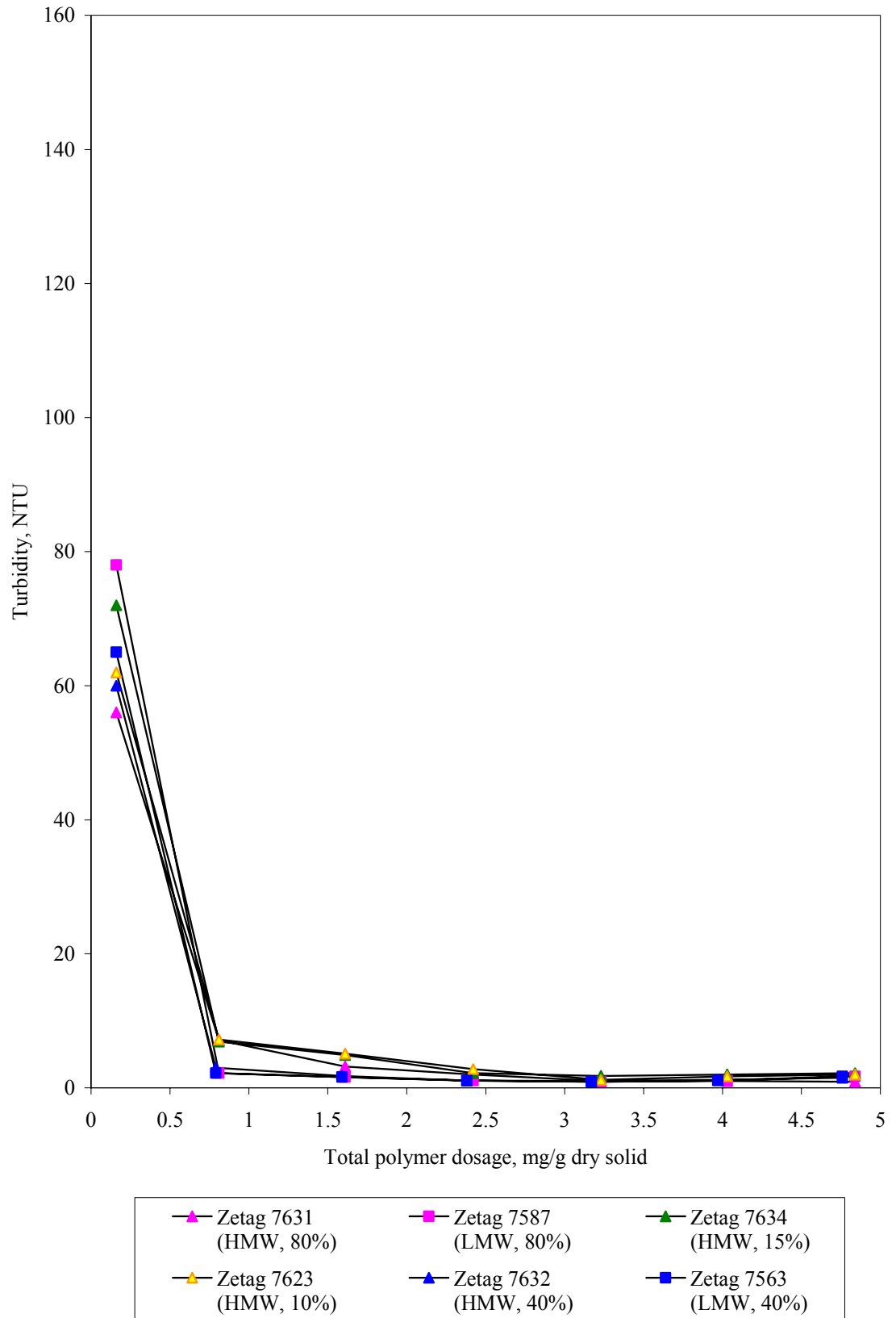
Figure 4.6. The supernatant turbidity of the sludge samples in the single conditioning with cationic polymers.
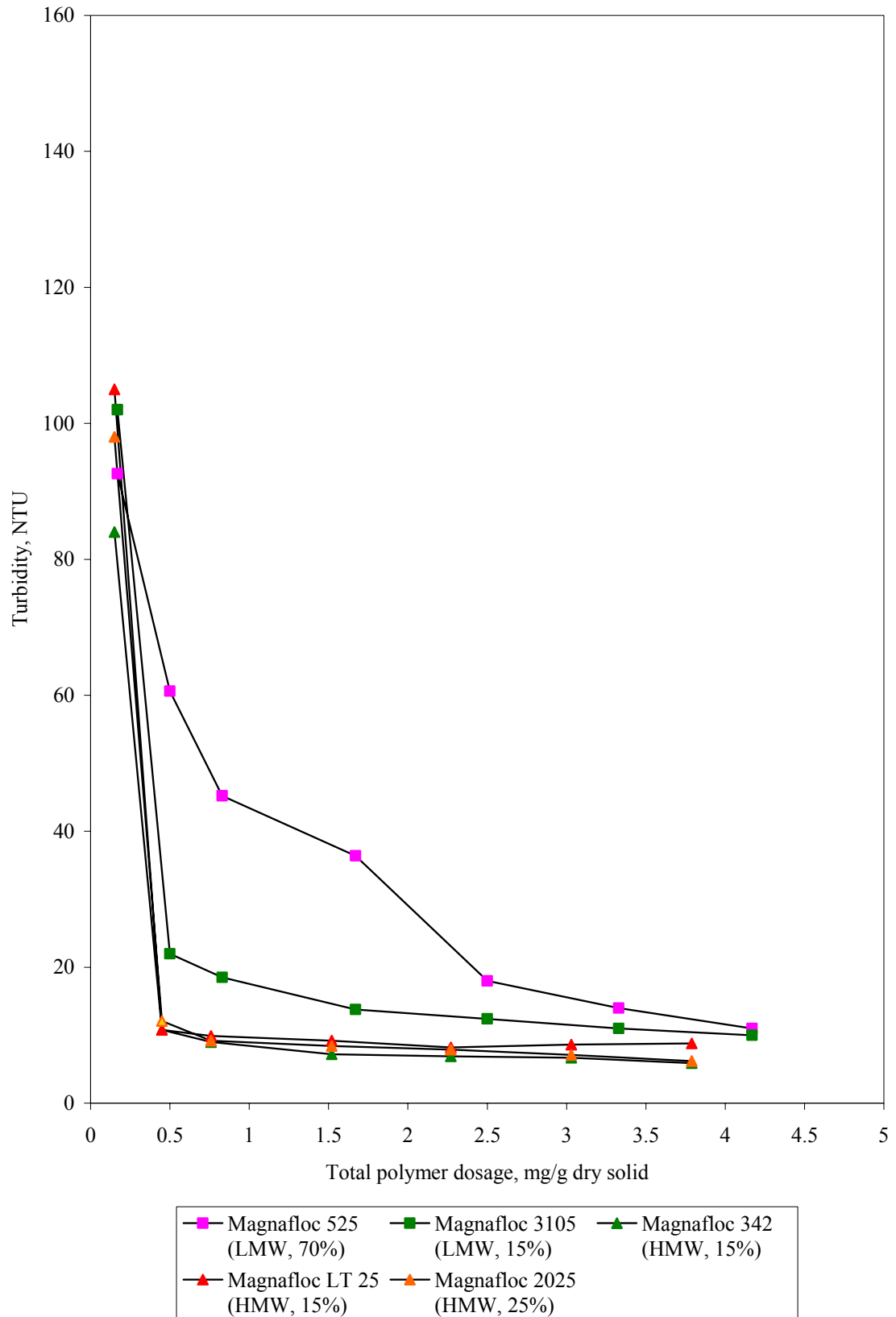
Figure 4.7. The supernatant turbidity of the sludge samples in the single conditioning with anionic polymers.
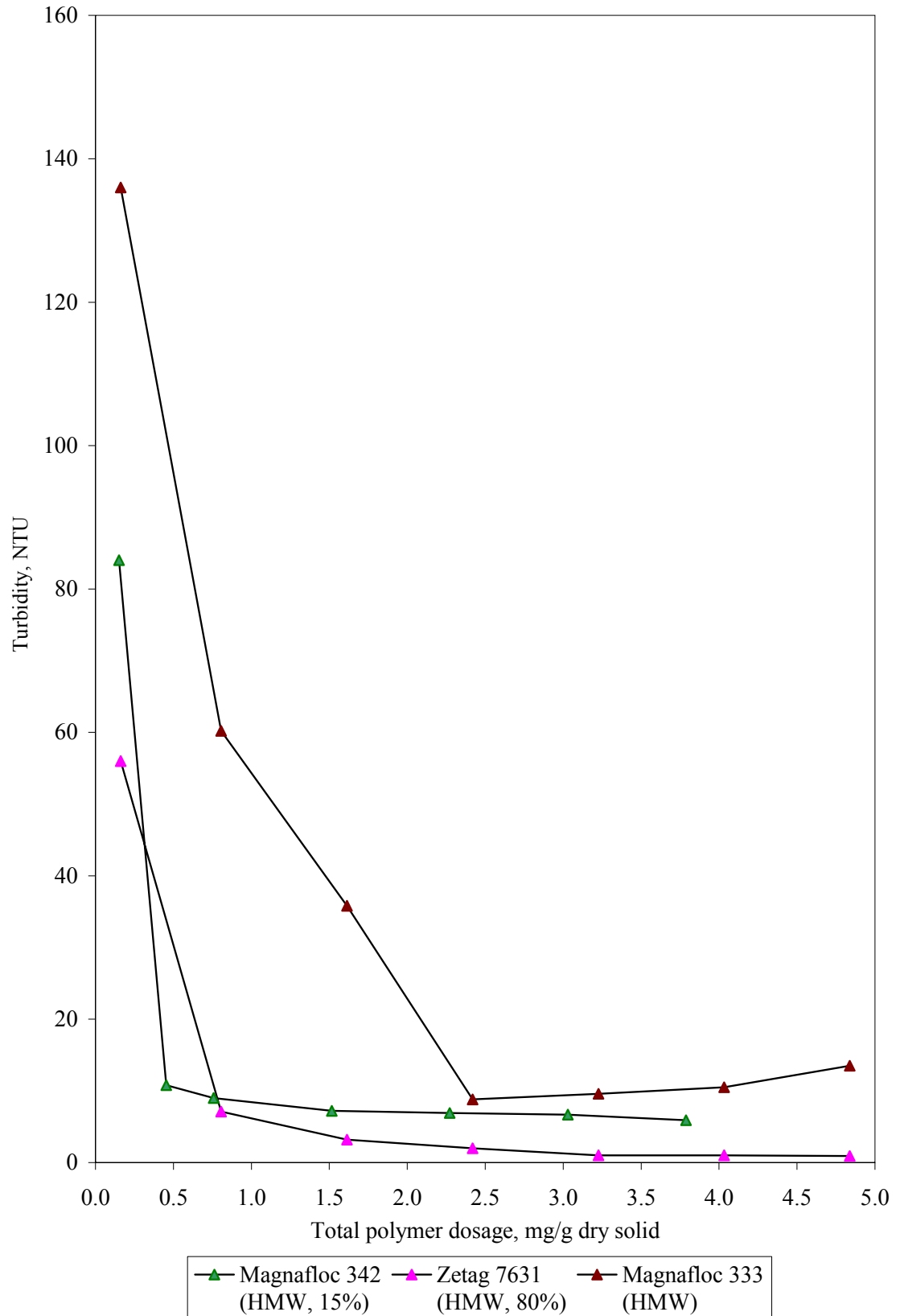
Figure 4.8. The supernatant turbidity curves for the best performing nonionic, cationic and anionic polymers in the single conditioning tests.

4.2. Dual Conditioning

In the dual conditioning tests, polymers were selected between the best performing ones in the single conditioning. The polymers are added into the sludge samples sequentially with an order given below.

- Cationic and cationic
- Cationic and anionic
- Cationic and nonionic
- Anionic and anionic
- Anionic and cationic
- Anionic and nonionic
- Nonionic and nonionic
- Nonionic and cationic
- Nonionic and anionic

In dual conditioning, polymers were added into the sludge samples sequentially with a ratio of 1:1. Following the first polymer addition, the sludge samples were mixed at 200 rpm for 120 s of rapid mixing. After the sequential addition of the second polymer, sludge samples were remixed at 200 rpm for 120 s of rapid mixing followed by slow mixing at 30 rpm for   300 s to promote flocculation.

4.2.1. Dual Conditioning with Cationic Polymers

Zetag 7631 and Zetag 7563 are high and low molecular weight cationic polymers. Senthilnathan and Sigler (1993) indicated that the dual conditioning with combinations of low and high molecular weight cationic polymers increased the solid content of the sludge cake and enhanced the solids capture and so reduced the blinding of the belt filter media. In agreement with Senthilnathan and Sigler (1993), Chitikela and Dentel (1998) showed that the use of the combinations low and high molecular weight cationic polymers enhanced the dewaterability of sludge. They observed that dual polymer conditioning

increased the solid content of sludge cake. Based on the results of this study, dual conditioning with low molecular weight cationic polymer followed by high molecular weight polymer did not improve the sludge dewaterability. The supernatant turbidity of the conditioned sludges is given in Figure 4.9. Figure 4.10. shows the relationship between the sludge dewaterability in dual conditioning and the total dosages of cationic polymers. Cationic polymers in both of single and dual conditioning were effective to capture the fine particles.
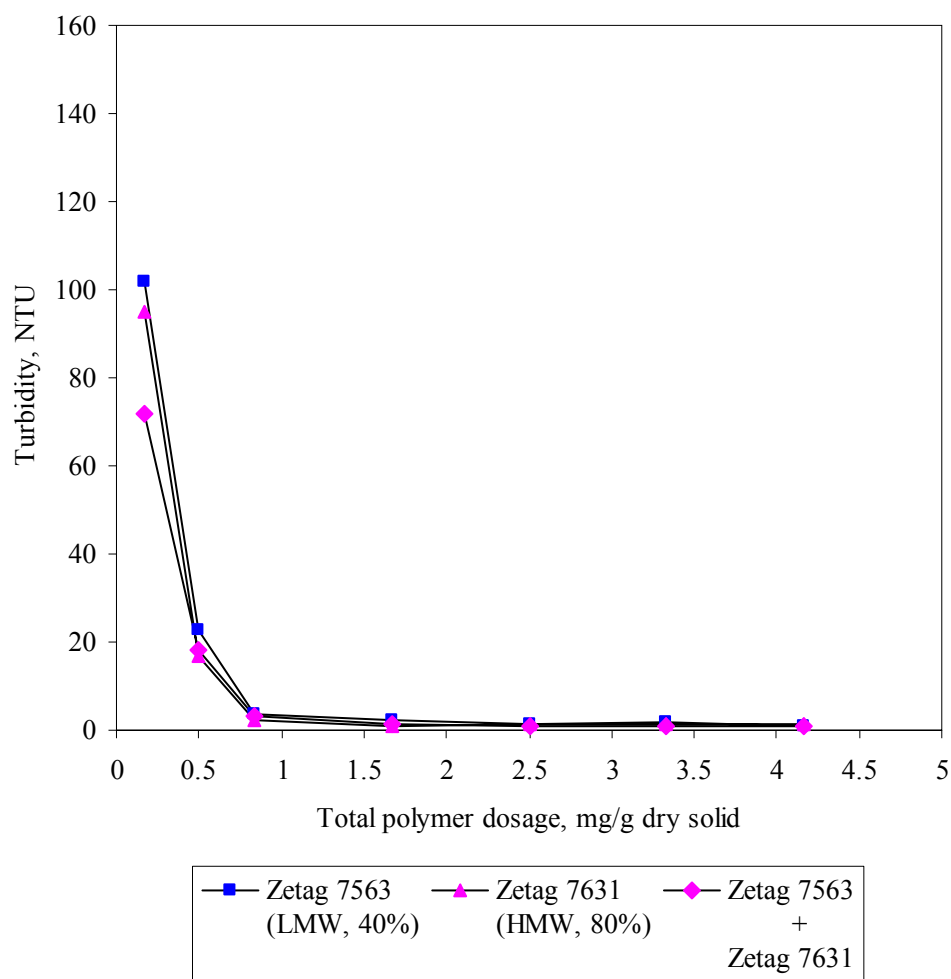
Figure 4.9. The supernatant turbidity of the sludge samples in the dual conditioning with cationic polymers.
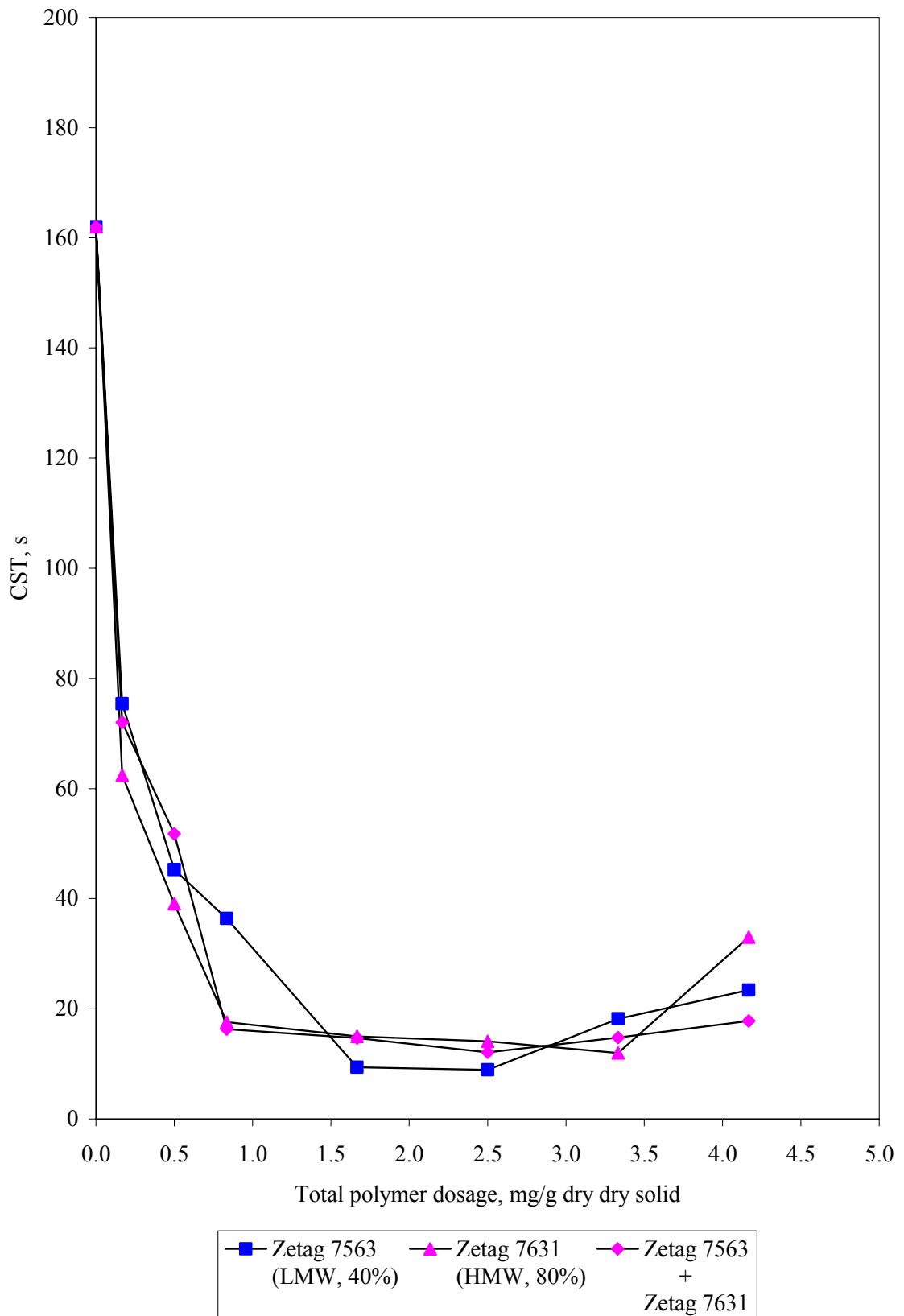
Figure 4.10. The relationship between dewaterability of dual conditioned sludge and the total dosage of cationic polymers of Zetag 7563 + Zetag 7631.

4.2.2. Dual Conditioning with Anionic Polymers

Magnafloc 3105 and Magnafloc 525, the low molecular weight polymers, were selected for the dual sludge conditioning with anionic polymers. Based on the results provided from the sludge dewaterability test, sludge preconditioned with anionic polymer followed by anionic polymer seemed not to provide relatively better dewatering than that of single conditioning. The supernatant turbidity of the conditioned sludges is given in Figure 4.11. Figure 4.12. shows the relationship between the sludge dewaterability in dual conditioning and the applied anionic polymer dosages. Anionic polymers in dual conditioning were not as effective as cationic polymers. Accordingly, the supernatant turbidities of the conditioned sludges were high.
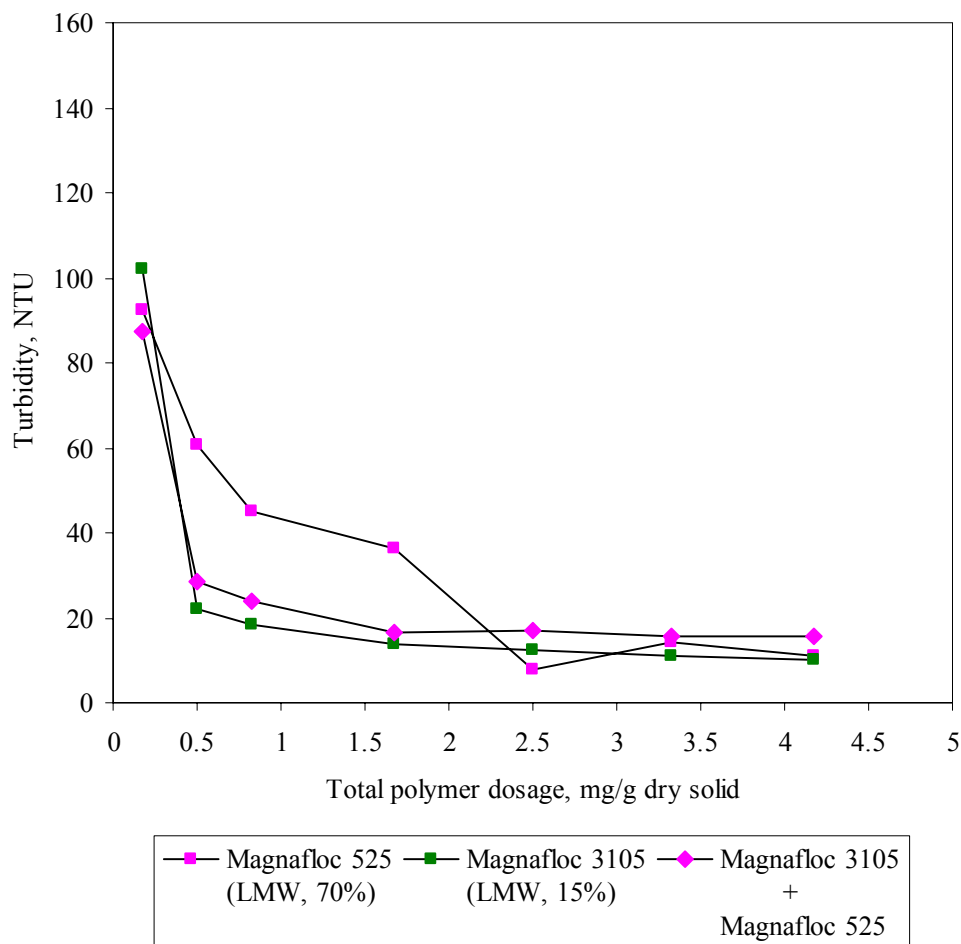

Figure 4.11. The supernatant turbidity of the sludge samples in the dual conditioning with anionic polymers.
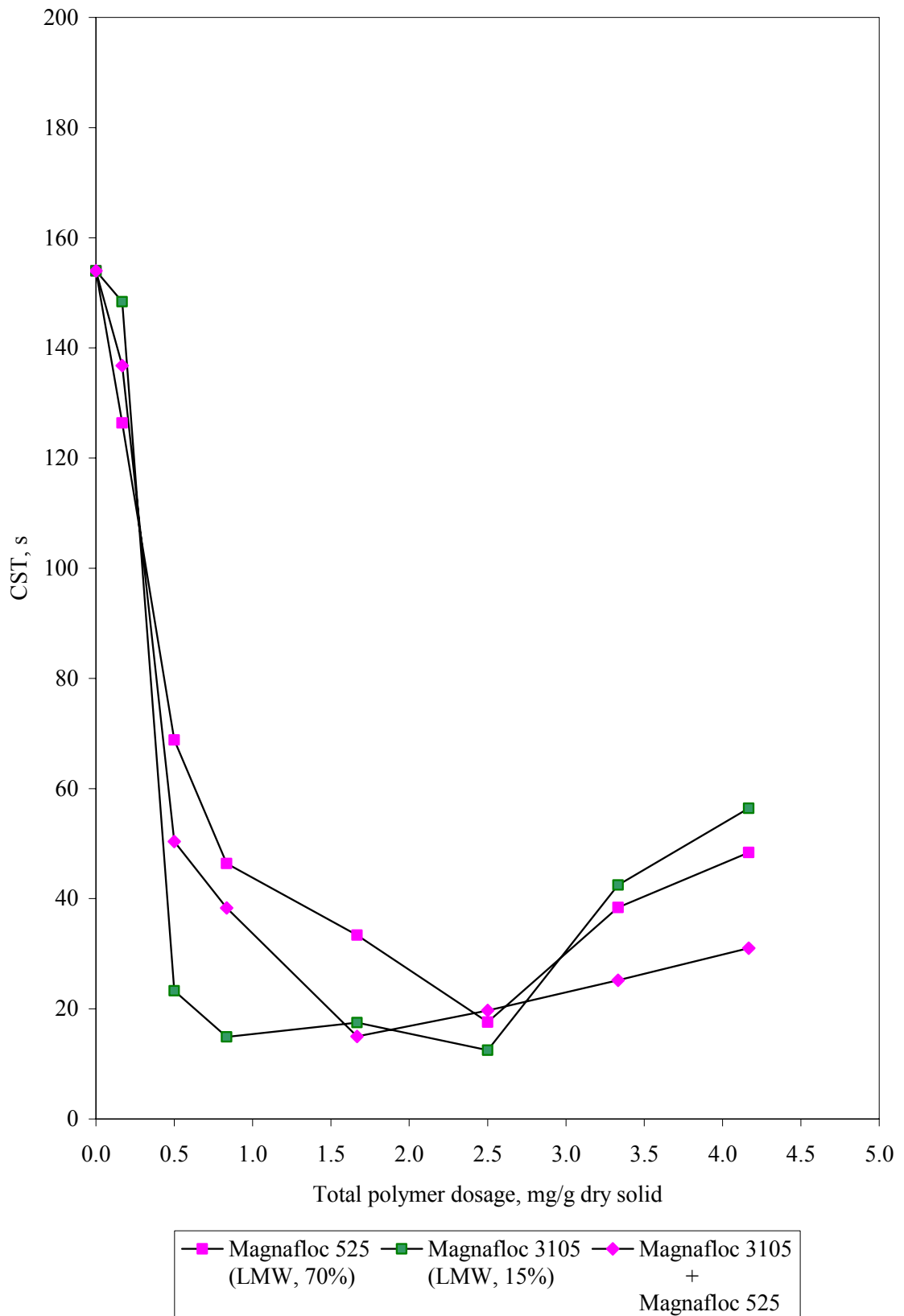
Figure 4.12. The relationship between dewaterability of dual conditioned sludge and the total dosage of anionic polymers Magnafloc 525 + Magnafloc 3105.

4.2.3. Dual Conditioning with Nonionic and Cationic Polymers

Dual conditioning experiments with nonionic and cationic polymers were carried out with Zetag 7631, Zetag 7587, Zetag 7634 and Magnafloc 333.

In dual conditioning, the lowest CST value of the sludge conditioned with Zetag 7631 followed by Magnafloc 333 was found to be 10.8 s at the polymer dosage of 2.42 mg/g dry solid. Even in the lower dosages of Zetag 7631 and Magnafloc 333, the CST values of sludge samples were lower than that of other sets of polymers. Figure 4.16., 4.17. and 4.18. show the relationship between the sludge dewaterability in dual conditioning and the applied cationic and nonionic polymer dosages.

Based on the dual conditioning test results, the dewaterability of the sludge sample preconditioned with cationic polymer followed by nonionic polymer resulted in better performance than that of preconditioned with nonionic polymer followed by cationic polymer. The results of this study showed that, a chance of overdosing in dual conditioning was less than that of single conditioning. Lee and Liu (2000) demonstrated that the sludge preconditioned with cationic polymer followed by nonionic polymer showed a better dewaterability, more efficient fine-particle capture with less chance of overdosing. In dual conditioning, when the cationic polymers were added into the sludge first, the more compact flocs were obtained compared to the addition of anionic or nonionic polymers first. It can be explained with the absorption of nonionic polymers on the loops and tails of cationic polymer by hydrogen bonding and Van der Waals forces leading to bridging of the primary flocs to form aggregates (Lee and Liu, 2000). On the other hand, sludge preconditioned with nonionic polymer first formed relatively larger, more fragile primary flocs. Lee and Liu (2000) state that the cationic polymers form complexes with the nonionic polymers and be adsorbed on primary flocs. However, the nonionic polymers were not as effective in the fine particle capture as the cationic polymers. That explains the reason of obtaining higher sludge turbidity values in dual conditioning with the nonionic polymer firsy and the cationic second. The supernatant turbidity value of the conditioned sludge is illustrated in Figure 4.13., Figure 4.14. and Figure 4.15.

Figure 4.13. The supernatant turbidity of the sludge samples in dual conditioning with Magnafloc 333 (nonionic) and Zetag 7631 (cationic).
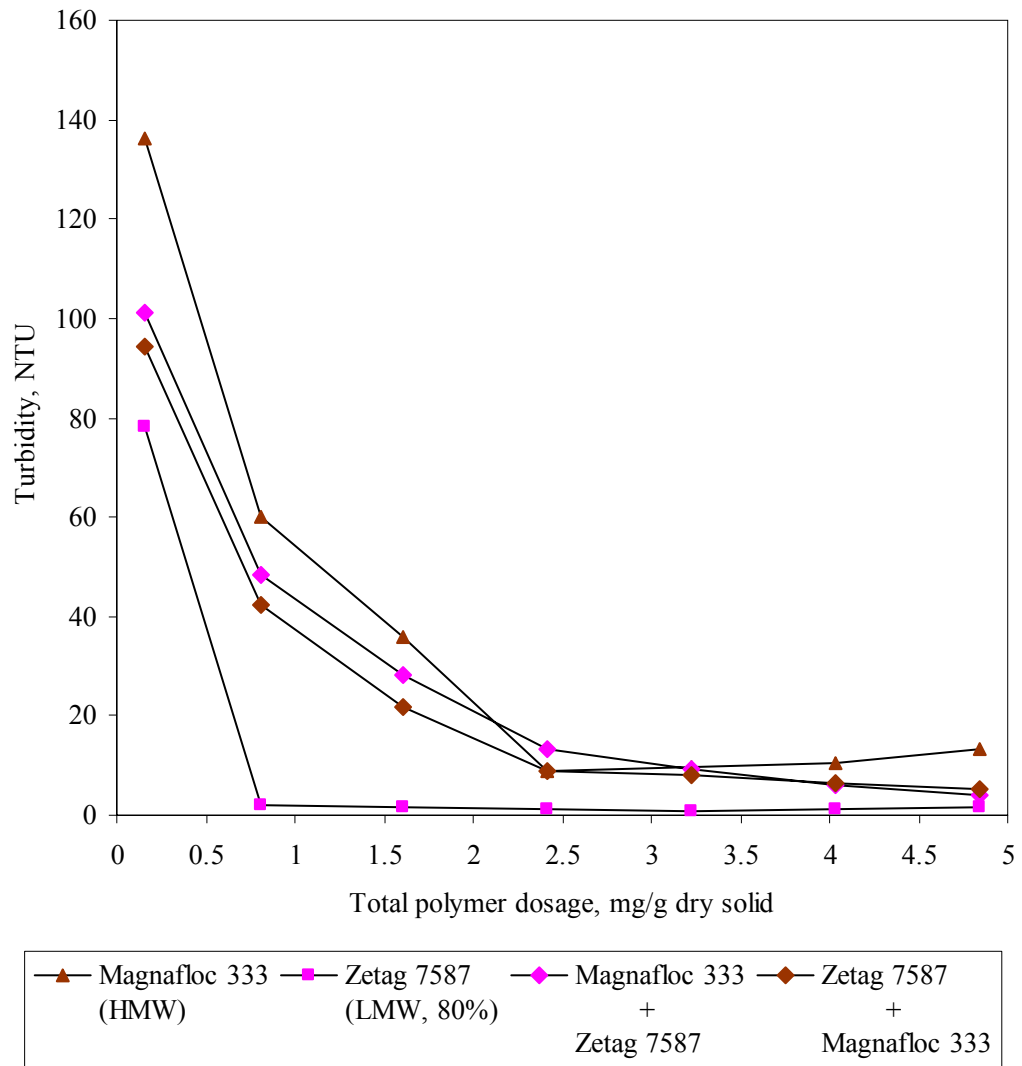
Figure 4.14. The supernatant turbidity of the sludge samples in dual conditioning with Magnafloc 333 (nonionic) and Zetag 7587 (cationic).
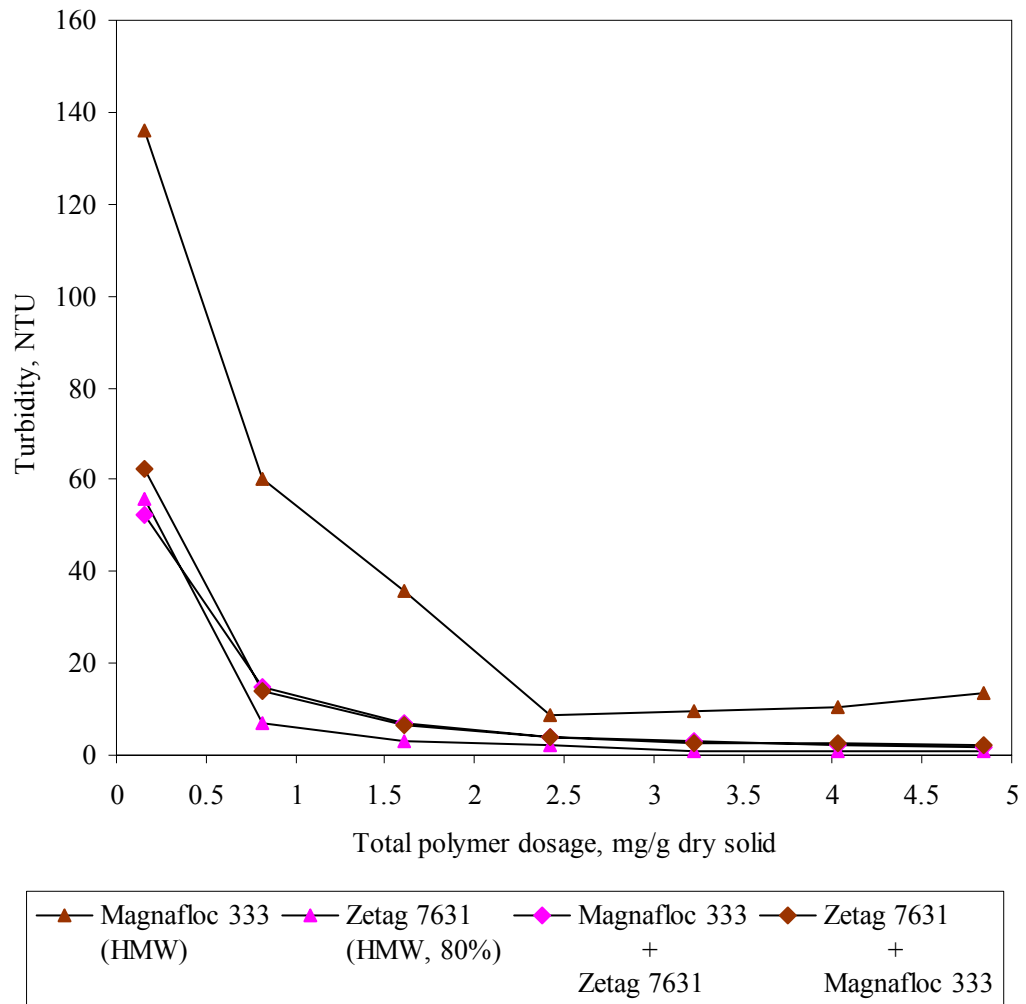
Figure 4.15. The supernatant turbidity of the sludge samples in dual conditioning with Magnafloc 333 (nonionic) and Zetag 7634 (cationic).
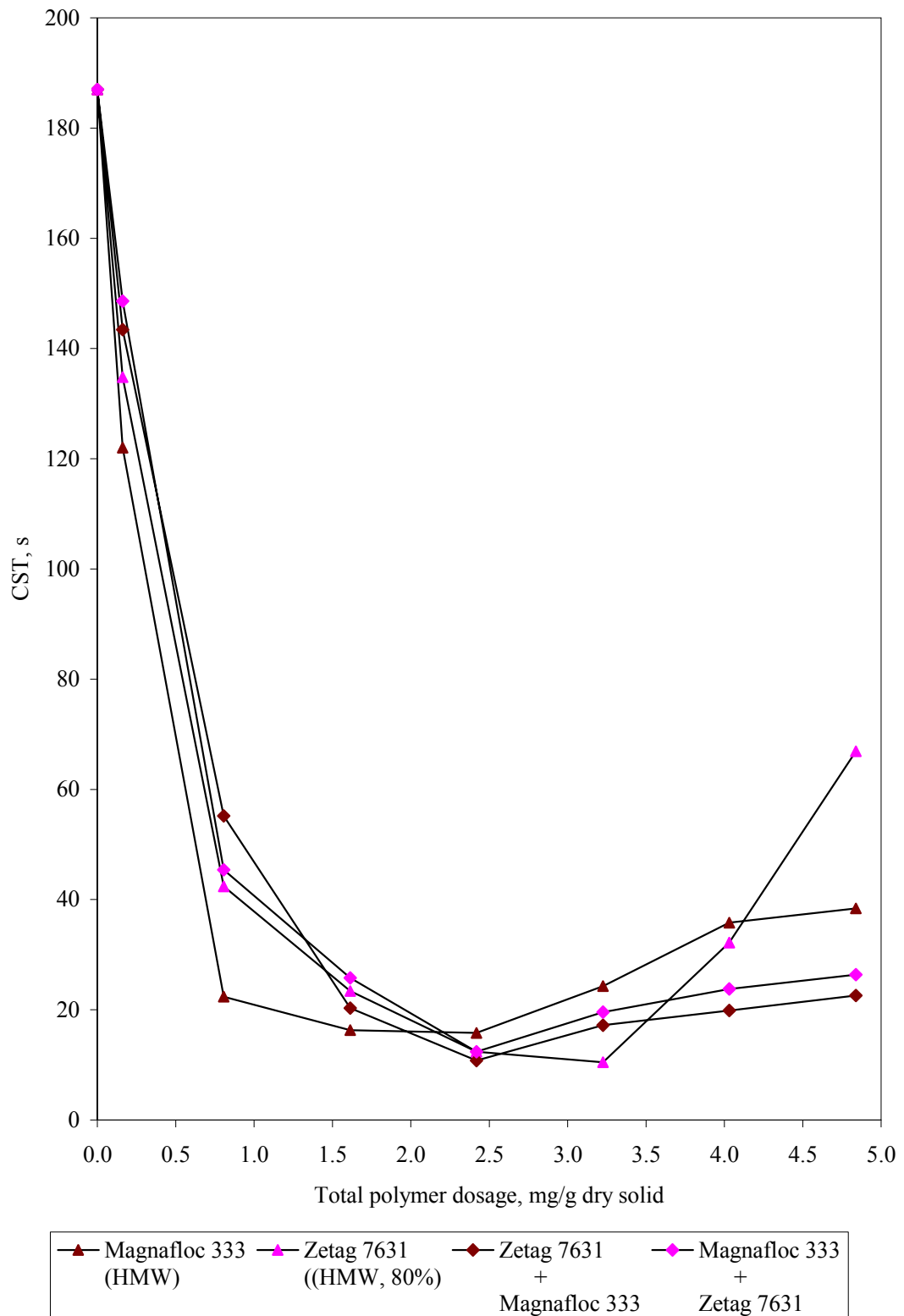
Figure 4.16. The relationship between dewaterability of dual conditioned sludge and the total polymer dosage of Zetag 7631 (cationic) + Magnafloc 333 (nonionic).
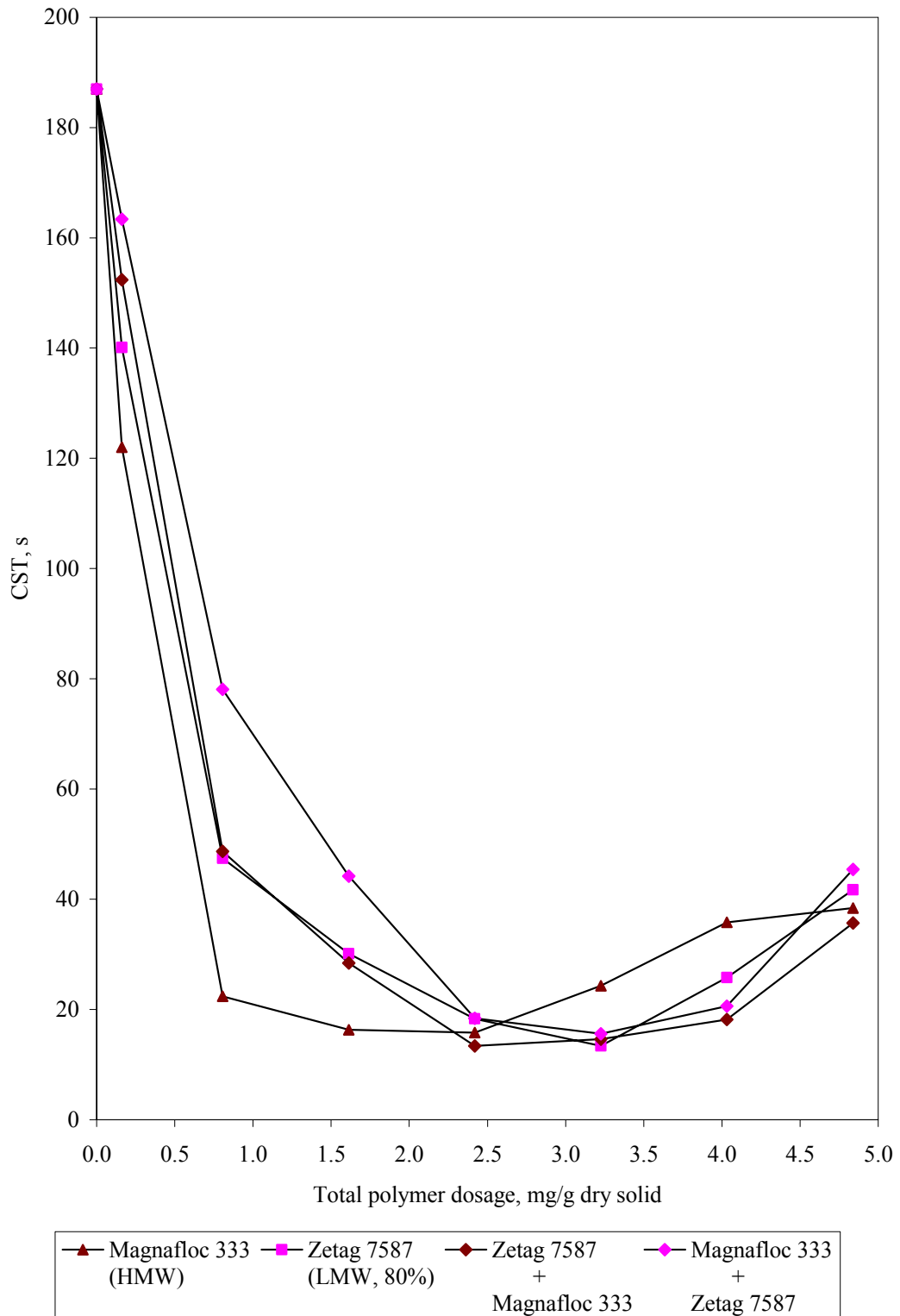
Figure 4.17. The relationship between dewaterability of dual conditioned sludge and the total polymer dosage of Zetag 7587 (cationic) + Magnafloc 333 (nonionic).
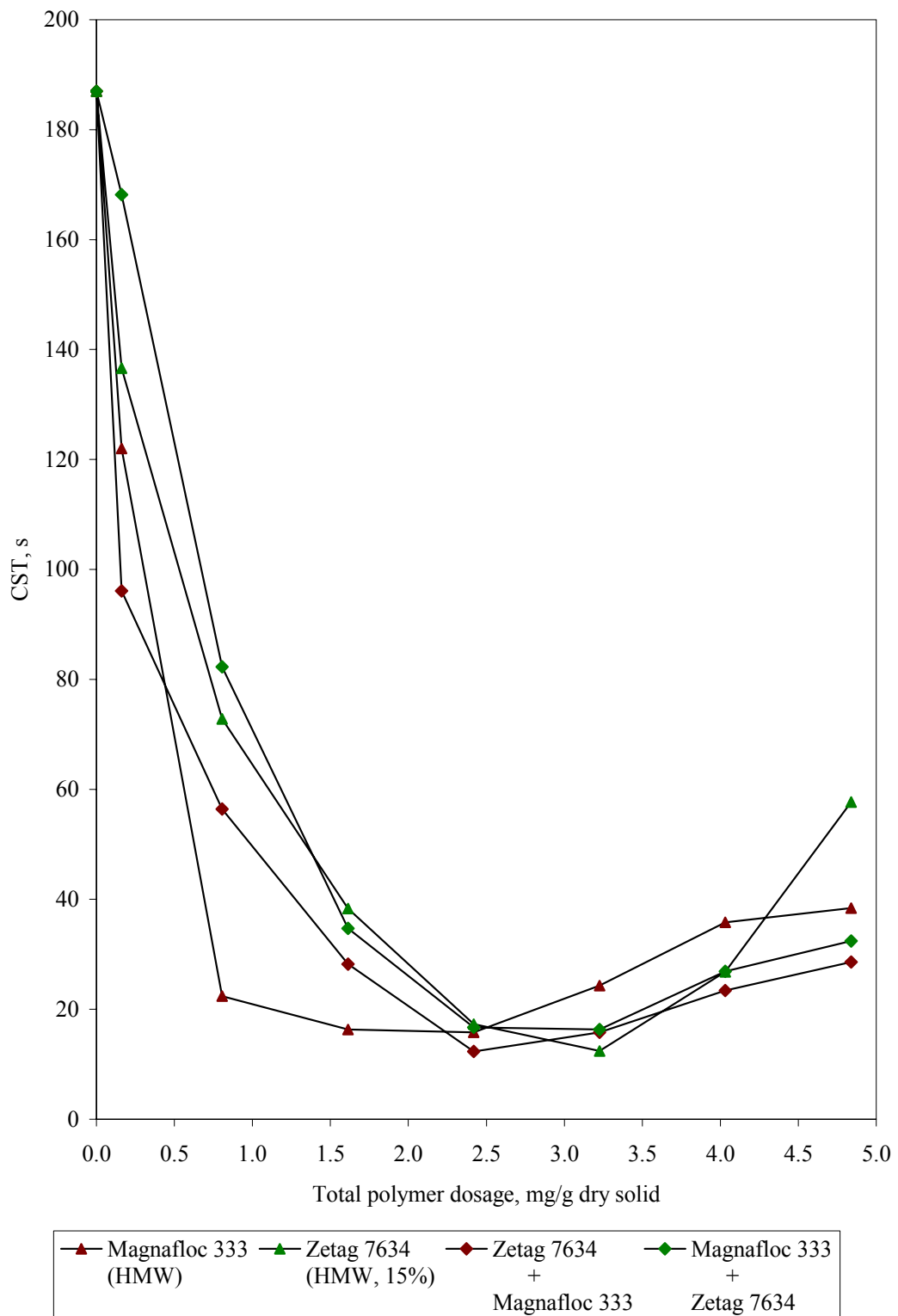
Figure 4.18. The relationship between dewaterability of dual conditioned sludge and the total polymer dosage of Zetag 7634 (cationic) + Magnafloc 333 (nonionic).

4.2.4. Dual Conditioning with Anionic and Cationic Polymers

In dual sludge conditioning tests, three polymers were selected to determine the sludge dewaterability. These are Zetag 7631, Magnafloc 3105 and Magnafloc 342.

In the dual conditioning of the sludge samples with Zetag 7631, Magnafloc 3105 and Magnafloc 342, the lowest CST values were reached when the sludges were preconditioned with anionic polymer followed by cationic polymer. Figure 4.22. and Figure 4.23. show the relationship between the sludge dewaterability of dual conditioned sludges and the total dosage of anionic and cationic polymer. The supernatant turbidity of the conditioned sludges is illustrated in Figure 4.19. Figure 4.20. Similar to our results, Ringqvist and Igsell (1994) obtained that the use of high molecular weight anionic and cationic polymers in combination enhanced the dewaterability of sludge. In addition, the dual polymer conditioning was found to be competitive from a cost point of view when compared to the single conditioning.

4.2.5. Dual Conditioning with Anionic and Nonionic Polymers

In this dual sludge conditioning set, high molecular weight polymers Magnafloc 342 and Magnafloc 333 were used as anionic and nonionic polymers respectively. In the literature, anionic and nonionic conditioning is the very unusual conditioning process. Anionic and nonionic polymers are especially used in the dual conditioning systems with the combination of cationic polymers. Based on our test results, there is no any advantage to use the combination of nonionic and anionic polymers in dual sludge conditioning, the relationship between the dewaterability of dual conditioned sludges and the total dosages of anionic and nonionic polymer is illustrated in Figure 4.24. The supernatant of the conditioned sludge samples were always turbid. The dewatering characteristic of the sludge conditioned with anionic and nonionic polymers was poor compared to sludges conditioned with cationic+anionic and cationic+nonionic polymers. The supernatant turbidity of the conditioned sludges is given in Figure 4.21.
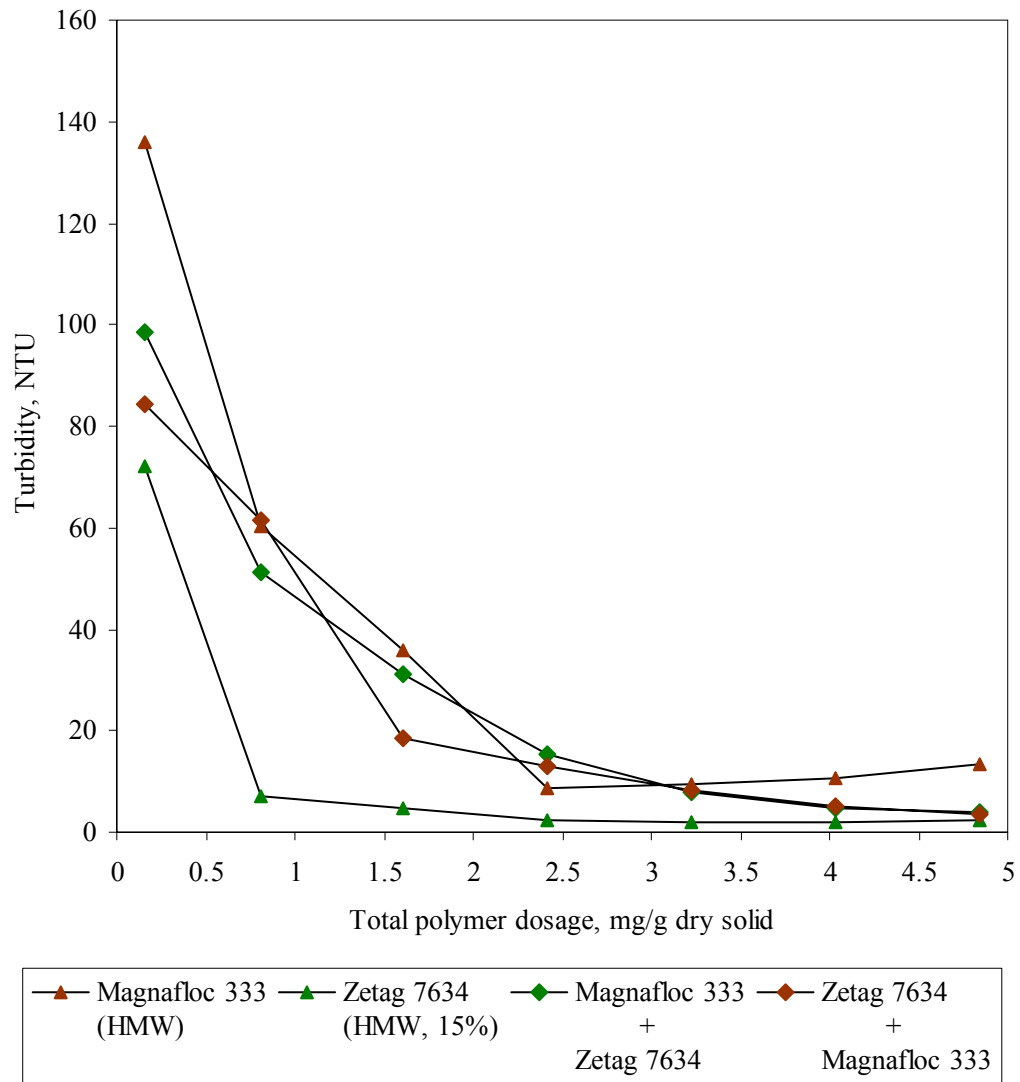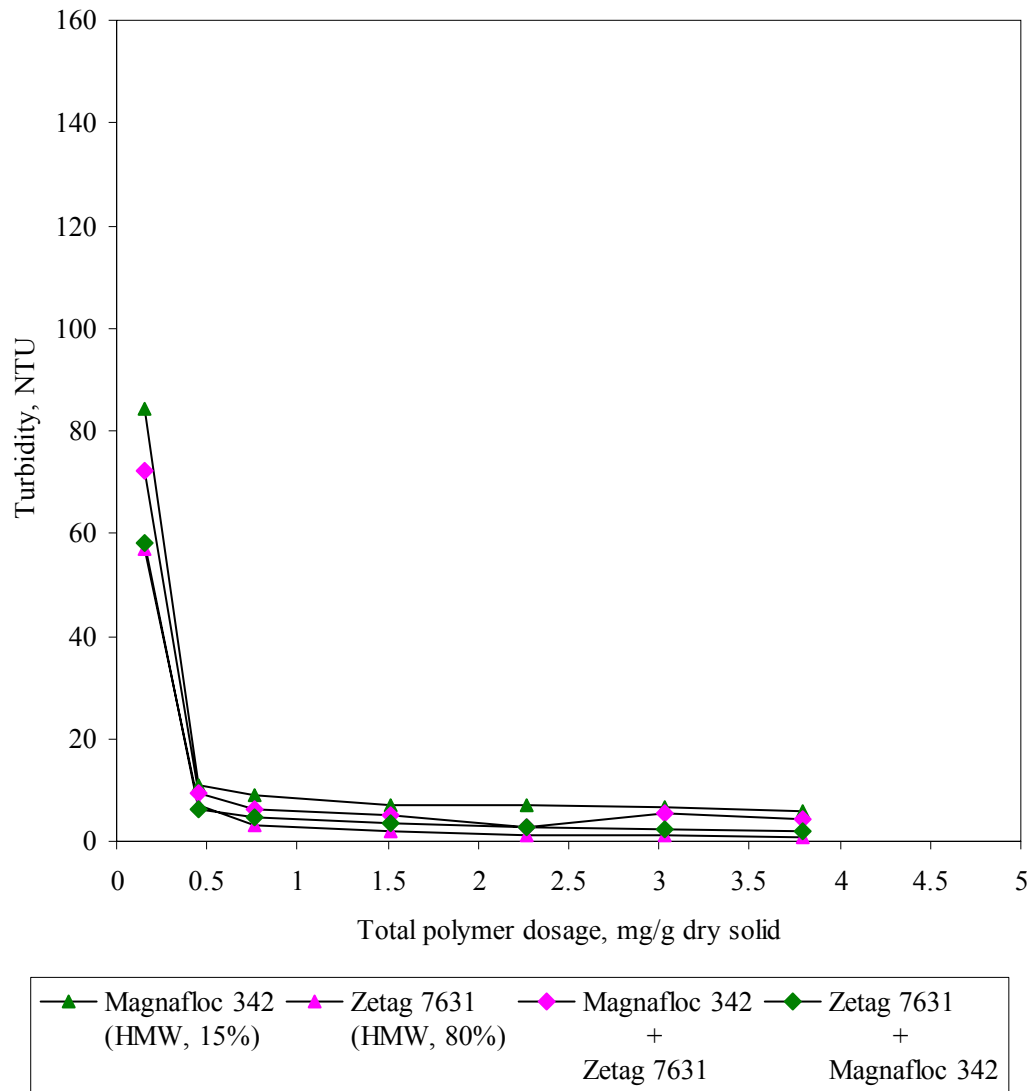
Figure 4.19. The supernatant turbidity of the sludge samples in dual conditioning with Magnafloc 342 (anionic) and Zetag 7631 (cationic).
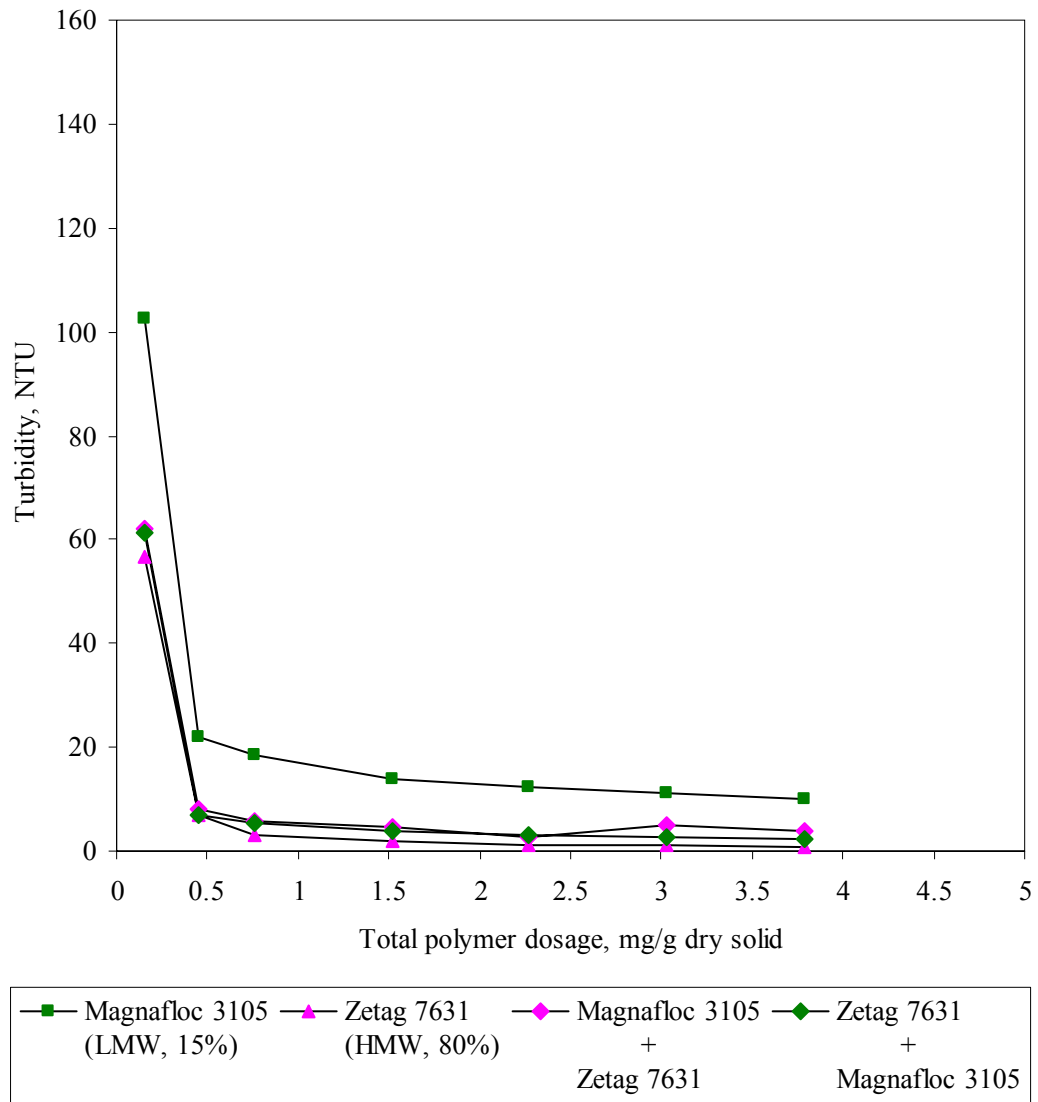
Figure 4.20. The supernatant turbidity of the sludge samples in dual conditioning with Magnafloc 3105 (anionic) and Zetag 7631 (cationic).
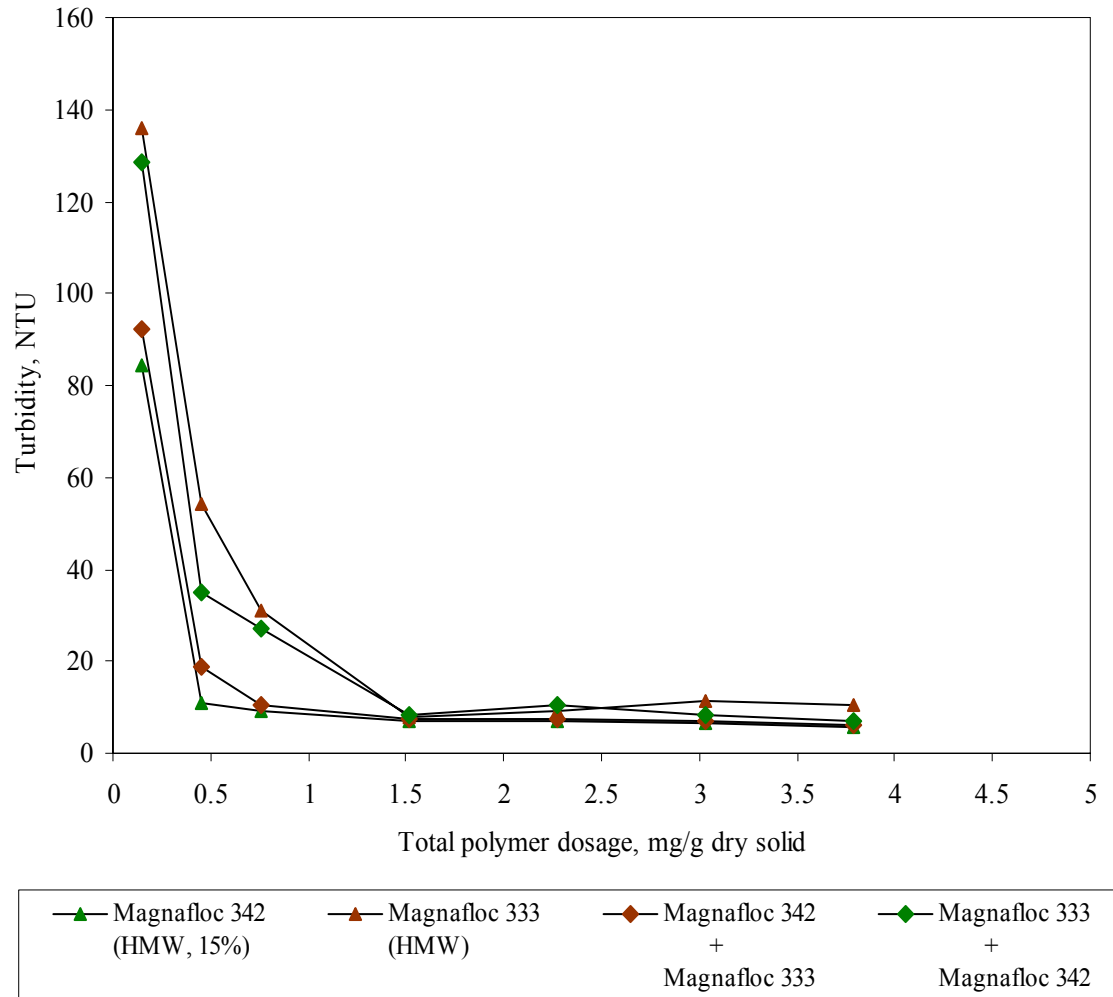
Figure 4.21. The supernatant turbidity of the sludge samples dual conditioned with Magnafloc 342 (anionic) and Magnafloc 333 (nonionic).
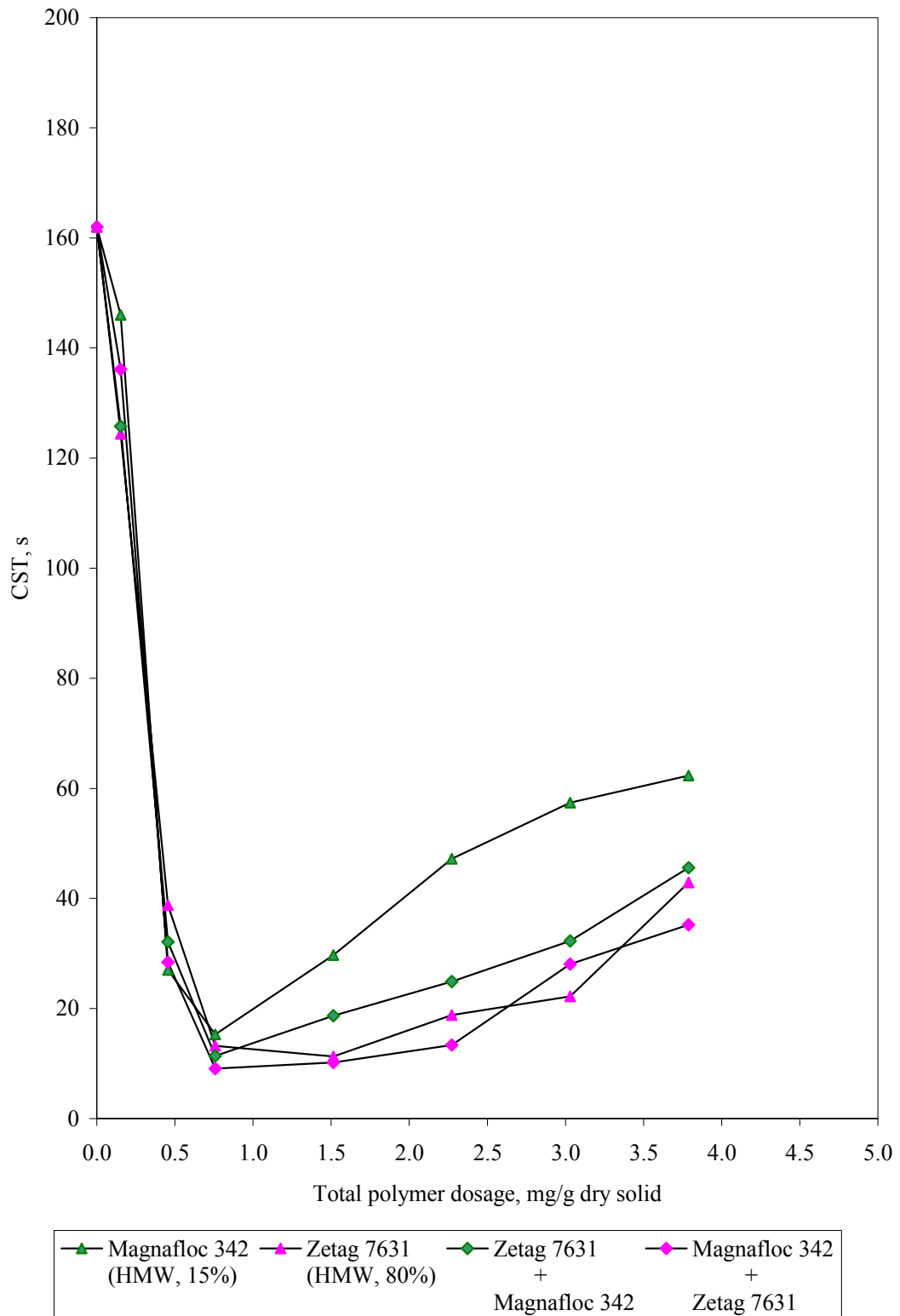
Figure 4.22. The relationship between dewaterability of dual conditioned sludge and the total polymer dosage of Magnafloc 342 (anionic) and Zetag 7631 (cationic).
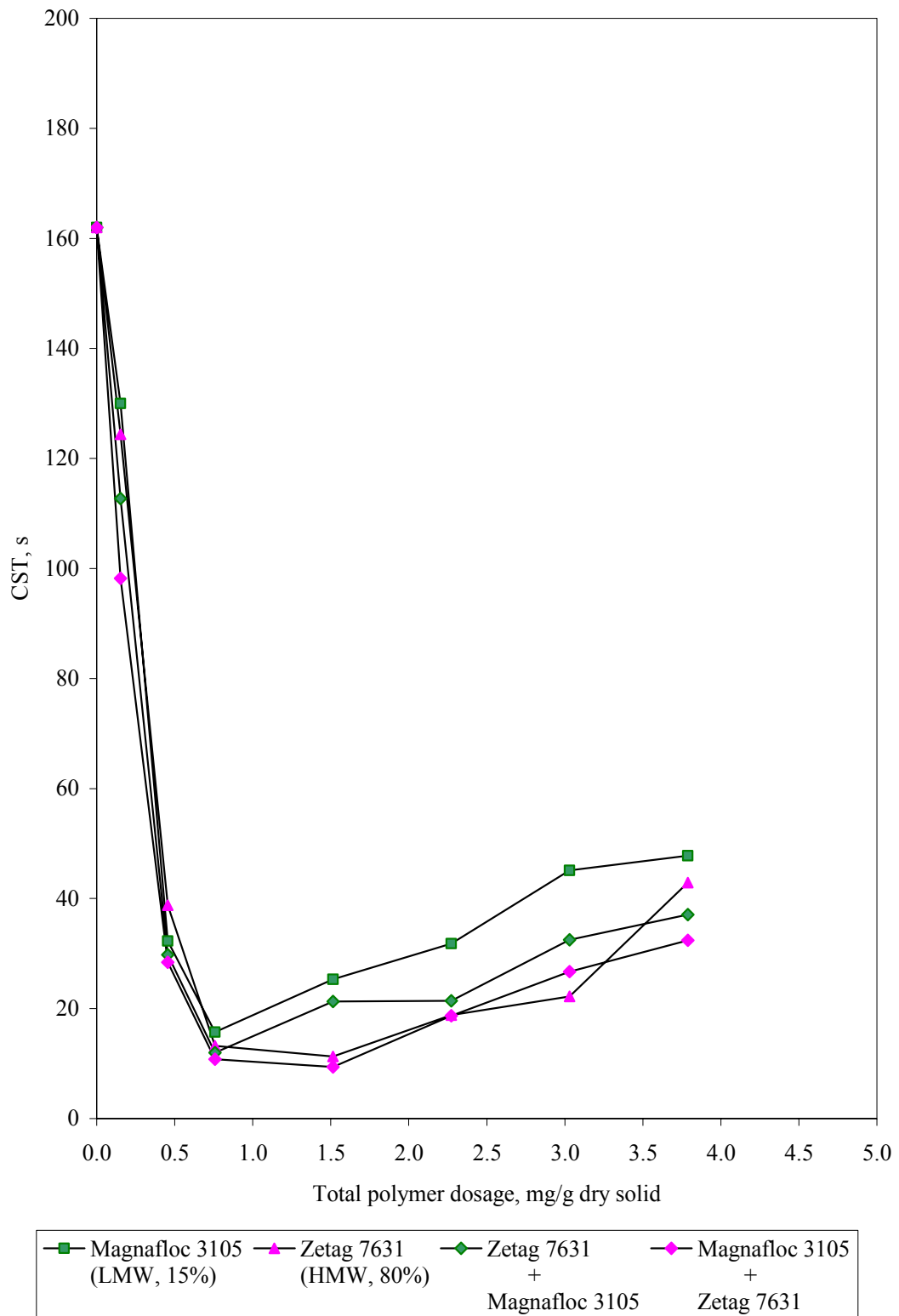
Figure 4.23. The relationship between dewaterability of dual conditioned sludge and the total polymer dosage of Zetag 7631 (cationic) and Magnafloc 3105 (anionic).
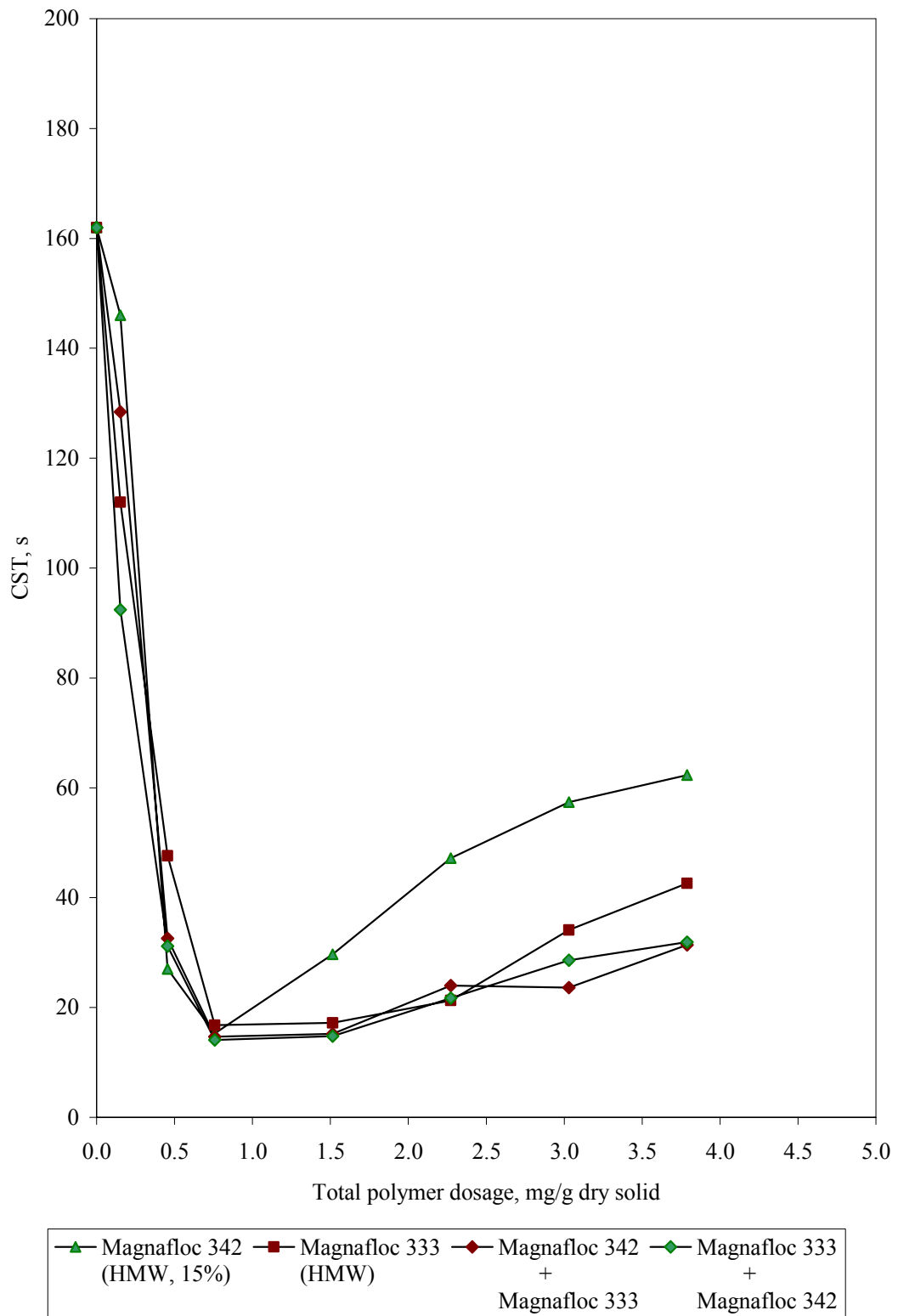
Figure 4.24. The relationship between dewaterability of dual conditioned sludge and the total polymer dosage of Magnafloc 333 (nonionic) and Magnafloc 342 (anionic)

4.3. Floc Structures of the Conditioned Sludge Samples

The change in the sludge floc structure after polymer conditioning was observed microscopically. Krüss Optronic MLB 2100 model microscope was used with achromatic lenses with an x4 eyepiece. The pictures of the raw sludge and single conditioned sludge samples are given in Figure 4.25. The selected pictures of the dual conditioned sludge samples are given in Figure 4.26., 4.27. and 4.28.
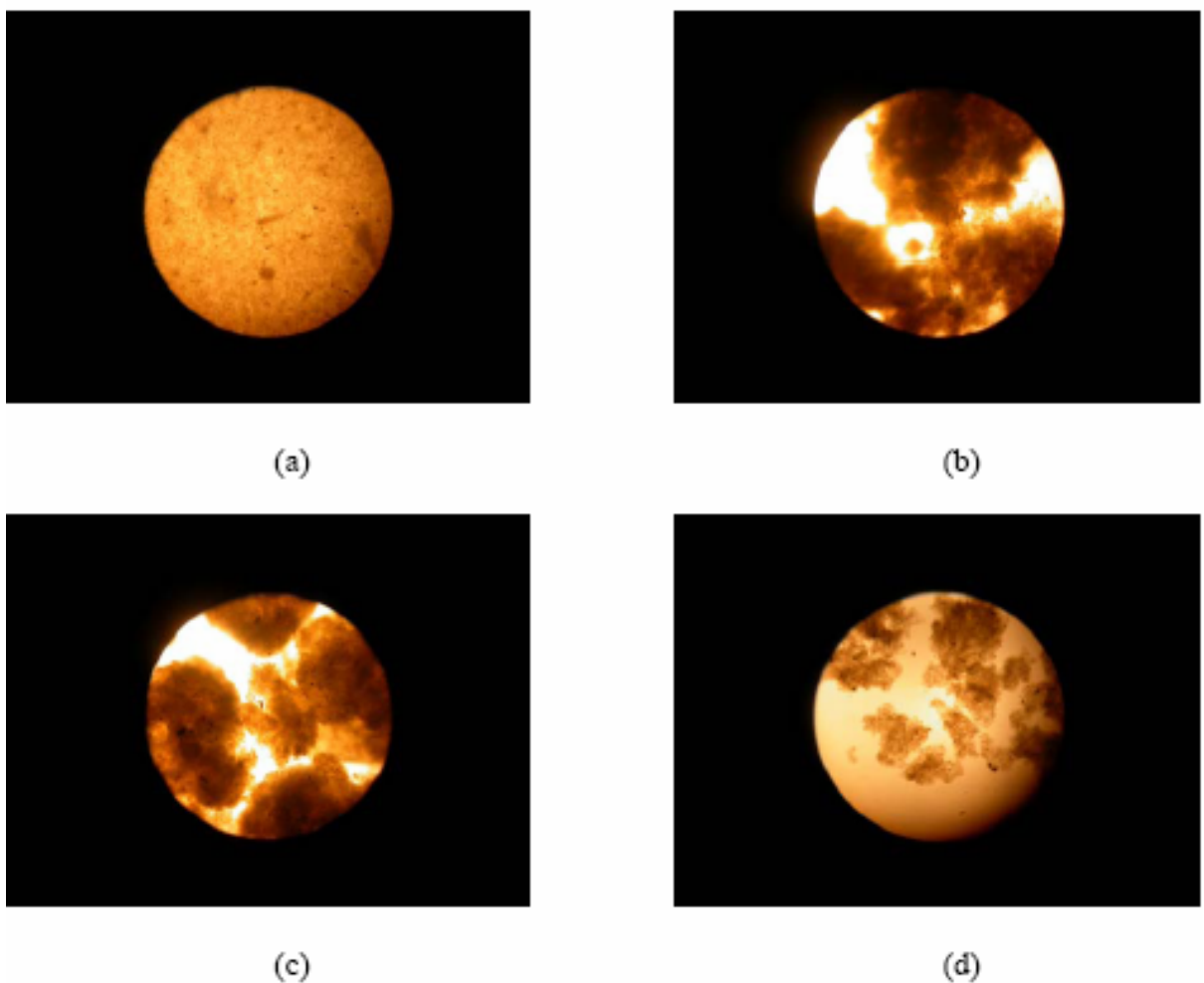
Figure 4.25. The picture of the raw sludge and the single conditioned sludge at the optimum polymer dosages (a) raw sludge, (b) Magnafloc 342 (anionic), (c) Magnafloc 333 (nonionic), (d) Zetag 7631 (cationic).

(a)

(b)
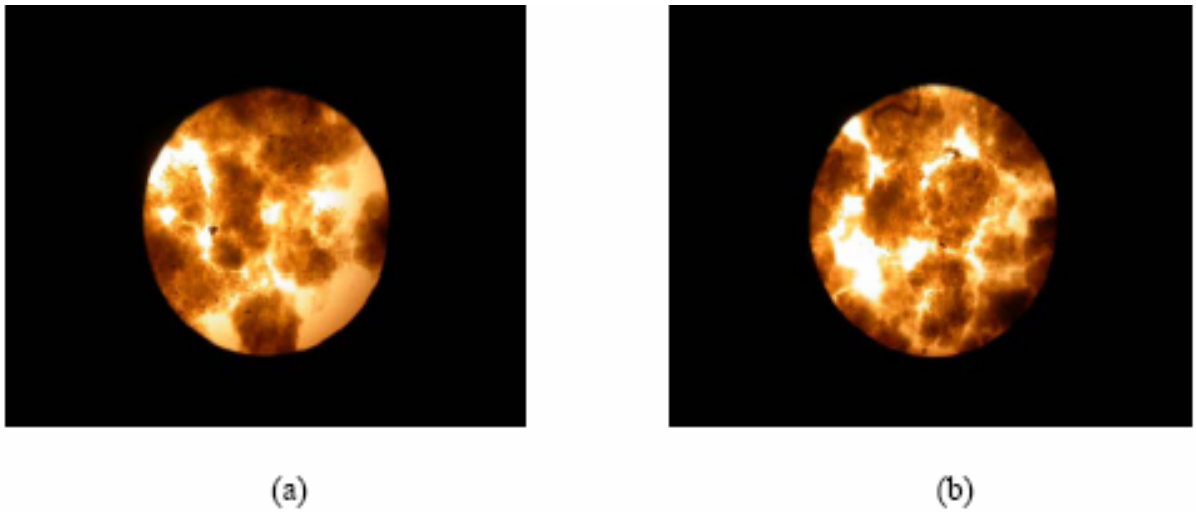
Figure 4.26. The picture of the dual conditioned sludge samples at the optimum polymer dosage of Magnafloc 333 (nonionic) + Magnafloc 342 (anionic),

(a) preconditioned with Magnafloc 333 followed by Magnafloc 342,

(b) preconditioned with Magnafloc 342 followed by Magnafloc 333.

(a)

(b)
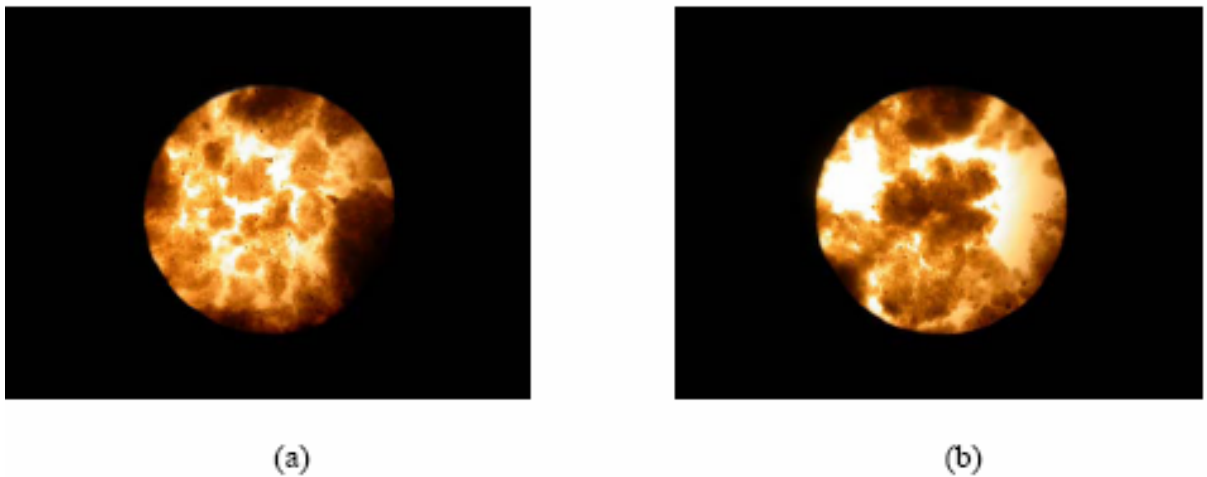
Figure 4.27. The picture of the dual conditioned sludge samples at the optimum polymer dosage of Magnafloc 333 (nonionic) + Zetag 7631 (cationic),

(a) preconditioned with Magnafloc 333 followed by Zetag 7631,

(b) preconditioned with Zetag 7631 followed by Magnafloc 333.
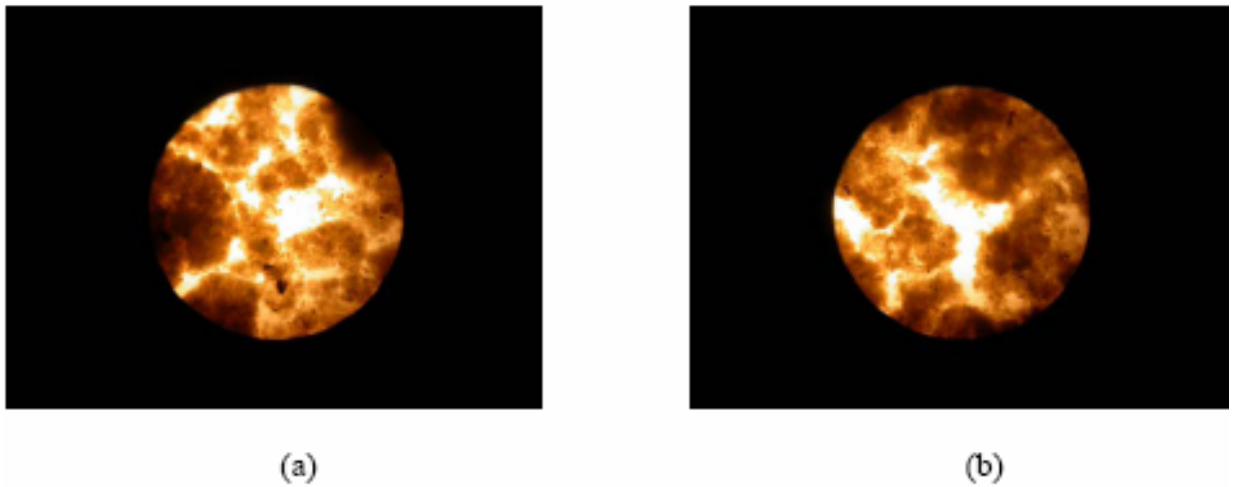
Figure 4.28. The picture of the dual conditioned sludge samples at the optimum polymer dosage of Magnafloc 342 (anionic) + Zetag 7631 (cationic),
(a) preconditioned with Magnafloc 342 followed by Zetag 7631,
(b) preconditioned with Zetag 7631 followed by Magnafloc 342.

In single conditioning, when the cationic polymer Zetag 7631 were added into the sludge, the more compact and uniform flocs were obtained. The flocs obtained from sludge samples conditioned with anionic polymer Magnafloc 342 and nonionic polymer Magnafloc 333 were relatively larger and non-uniform in size.

In dual conditioning, the sludge samples preconditioned with anionic Magnafloc 342 polymer followed by nonionic polymer Magnafloc 333 and visa versa addition of these two polymers, the size of the flocs were much larger that of sludge conditioned with cationic+anionic and cationic+nonionic polymers. When the cationic polymer Zetag 7631 were added into the sludge first, the more compact flocs were obtained compared to the addition of anionic or nonionic polymers first.

Çetin and Erdinçler (2004) stated that filterability and compactibility of sludges improved by the increase of the size and strength of the flocs.

4.4. Rheological Behavior of the Sludge Samples

Sludges are particularly difficult materials to characterize in a quantitative manner. The rheological measurements are very useful in understanding wastewater treatment performance. Sludges from water and wastewater treatment plant processes are recognized as displaying thixotropic behavior (reduced viscosity with increasing shear). In this study, the rheology measurements of the conditioned sludge samples were performed by using a HAAKE RheoStress1 Rheometer. The rheometer was operated by the using a software program RheoWin Pro 2.91. This instrument is capable of measuring the shear stress at different controlled shear rates. All rheology measurements were obtained at a constant temperature of 25°C. The shear rate was increased from 0 to 100 s^{-1} in 60 s. This acceleration rate provided distinctive peaks in the produced rheograms for the conditioned sludge samples.

Based on the result of this study, in single conditioning, when the cationic polymer Zetag 7631 was added into the sludge sample, the highest intial peak value (108.81 Pa) was obtained compared to the addition of anionic polymer Magnafloc 342 and nonionic polymer Magnafloc 333. Some researchers accept this peak as an equivalent to a yield stress. However, increase in the shear rates leads to a decrease in shear strength, probably due to the disruption of the conditioned sludge flocs. Zetag 7631 had the high apparent viscosity at the low shear rate. This result indicated that more energy was needed to break the floc bonds.

Abu-Orf and Dentel (1999) stated that the significantly higher shear stress values of the conditioned samples showed the stronger floc formation, resulting in the poor dewaterability due to the rapid clogging properties. Zetag 7631 caused to the highest shear stress value leading to poor sludge dewaterability. Figure 4.29 shows the rheograms obtained from controlled shear rate tests by using the polymers which were selected the best performing ones in the single sludge conditioning. No initial peak value was observed in the rheogram for the raw sludge sample. The initial peak values of the conditioned sludge samples are given in Table 4.3.

In dual conditioning, the shear stress values of the sludge samples conditioned with cationic+anionic and cationic+nonionic were lower than the single conditioning of cationic polymer Zetag 7631. This showed that the shear stress value in dual conditioning decreased as the cationic polymer dosage decreased. This situation resulted in the improving dewaterability by decreasing the clogging property of the cationic polymer Zetag 7631. The rheogram for single conditioned sludge samples are given in Figure 4.29. The rheograms of the dual conditioned sludge samples are given in Figure 4.30. through Figure 4.35.

Based on the rheological data, cationic polymers were added into the sludge sample, the highest shear stress was obtained. The higher shear stress value of the conditioned samples showed that stronger floc formation, resulting in the poor dewaterability due to the rapid clogging properties. More energy was needed to break the floc bonds.

Table 4.3. The initial peak values and the shear rate at critical peak of the conditioned sludge samples

Polymers	Initial peak value, Pa	Shear rate at the initial peak, s^{-1}
Zetag 7631	108.81	5.083
Magnafloc 342	64.87	3.530
Magnafloc 333	45.92	3.890
Magnafloc 333 + Magnafloc 342	49.95	3.679
Magnafloc 333 + Zetag 7631	52.33	3.762
Magnafloc 342 + Magnafloc 333	88.33	4.474
Zetag 7631 + Magnafloc 333	62.54	3.185
Zetag 7631 + Magnafloc 342	73.58	2.768
Magnafloc 342 + Zetag 7631	106.67	5.273

Abu-Orf and Dentel (1999) suggested that the results of the rheological data defined the optimum dose for conditioning. Stronger flocs, as indicated from the initial yield stress of the conditioned sludge samples, were not desirable for good dewaterability. Stronger flocs tend to hold more the trapped water between the flocs parts in dewatering process (Abu-Orf and Dentel, 1999). On the other hand, weaker flocs may yield more of this trapped water when dewatered resulting in better dewaterability. Campbell and Crescuolo (1982) used to the shear stress versus the shear rate curve of conditioned sludge for optimization of chemical conditioning through feedback control. They showed that the initial yield stress for the sludge increased as the polymer dosage increased, an initial peak became evident. They also concluded that the optimum polymer dose corresponded to a specific height for this peak. Otsubo (1990) observed that the initial peak of the conditioned sludge samples was attributed to the existence of the elastic floc network. The peak itself indicates the point at which the network bonds break. The higher initial peak value indicates the more energy needed to rupture the floc structure bonds. Gregory (1983) stated that flocs were broken up as a result of the applied shear. Flocs were not reformed, when the restabilization occurred.

Company	ORGANIK KIMYA	Measure device	RS1		
Operator	FULYA KORAY	Temperature device			
Date/Time		Sensor	C35/2° Ti	Gap	0.105 mm
Substance		A-factor	89059.000 Pa/Nm		
Sample no		M-factor	28.840 (1/s)/(rad/s)		
Description					

Comment

Filename: C:\Program Files\RheoWin\OLD\Data\Sludge\Raw Sludge.rwd (Mod)

Job: C:\Program Files\RheoWin\Jobs\Thixotrophy\RheoTest.rwj

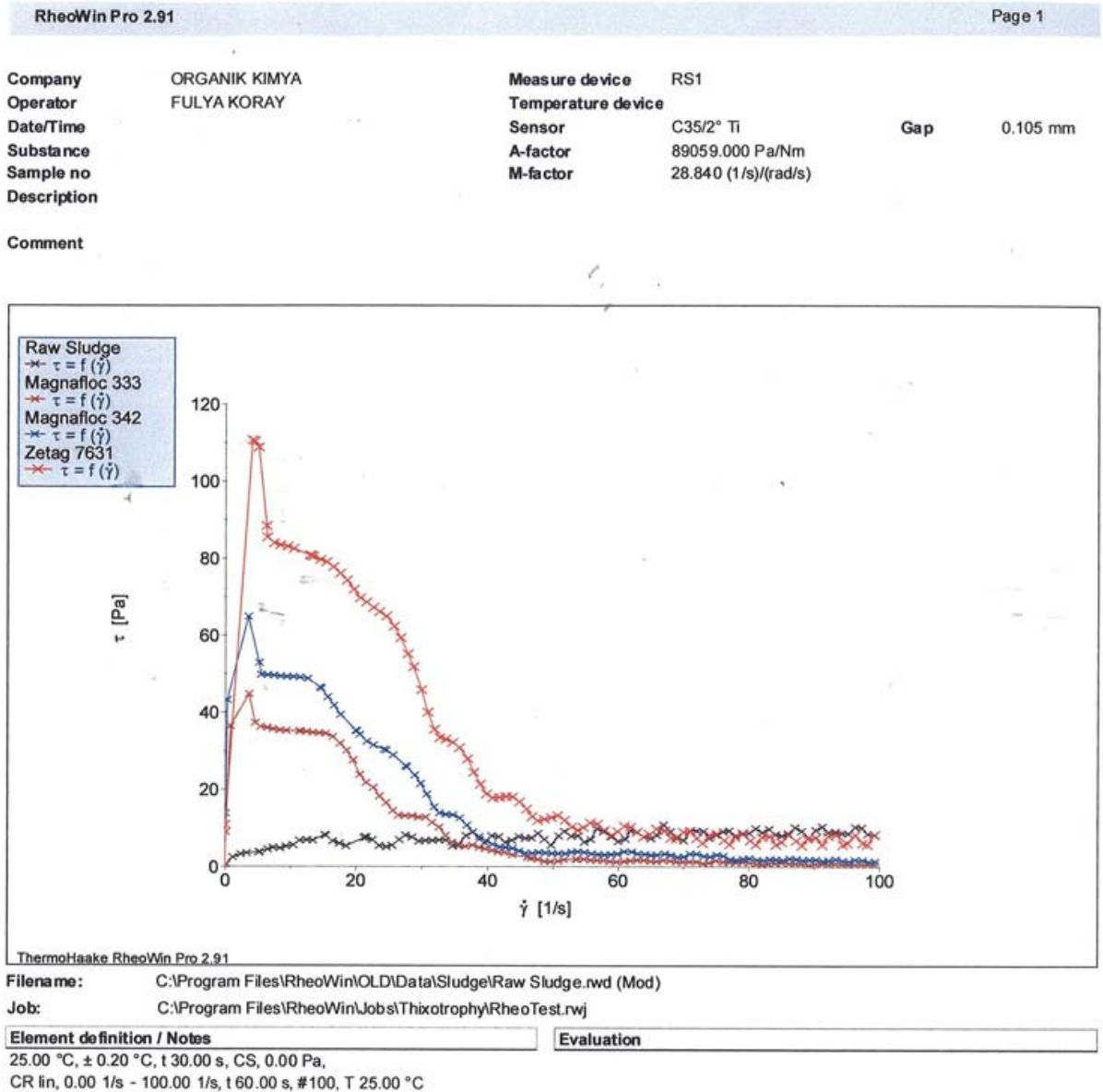| Element definition / Notes	Evaluation
25.00 °C, ± 0.20 °C, t 30.00 s, CS, 0.00 Pa, CR lin, 0.00 1/s - 100.00 1/s, t 60.00 s, #100, T 25.00 °C	

Figure 4.29. Rheogram for single conditioned sludge samples.

Figure 4.30. Rheogram for dual conditioned sludge with Zetag 7631 (cationic) + Magnafloc 333 (nonionic).

Figure 4.31. Rheogram for dual conditioned sludge with Magnafloc 333 (nonionic) + Zetag 7631 (cationic).

Company	ORGANIK KIMYA		Measure device	RS1		
Operator	FULYA KORAY		Temperature device			
Date/Time			Sensor	C35/2° Ti	Gap	0.105 mm
Substance			A-factor	89059.000 Pa/Nm		
Sample no			M-factor	28.840 (1/s)/(rad/s)		
Description						

Comment

Magnafloc 333
τ = f (γ̇)
Magnafloc 333 + Magnafloc 342
τ = f (γ̇)
Magnafloc 342 + Magnafloc 333
τ = f (γ̇)

ThermoHaake RheoWin Pro 2.91

Filename: C:\Program Files\RheoWin\OLD\Data\Sludge\Magnafloc 333.rwd

Job: C:\Program Files\RheoWin\Jobs\Thixotrophy\RheoTest.rwj

Element definition / Notes   Evaluation

25.00 °C, ± 0.20 °C, t 30.00 s, CS, 0.00 Pa,
CR lin, 0.00 1/s - 100.00 1/s, t 60.00 s, #100, T 25.00 °C

Figure 4.32. Rheogram for dual conditioned sludge with Magnafloc 333 (nonionic) + Magnafloc 342 (anionic).

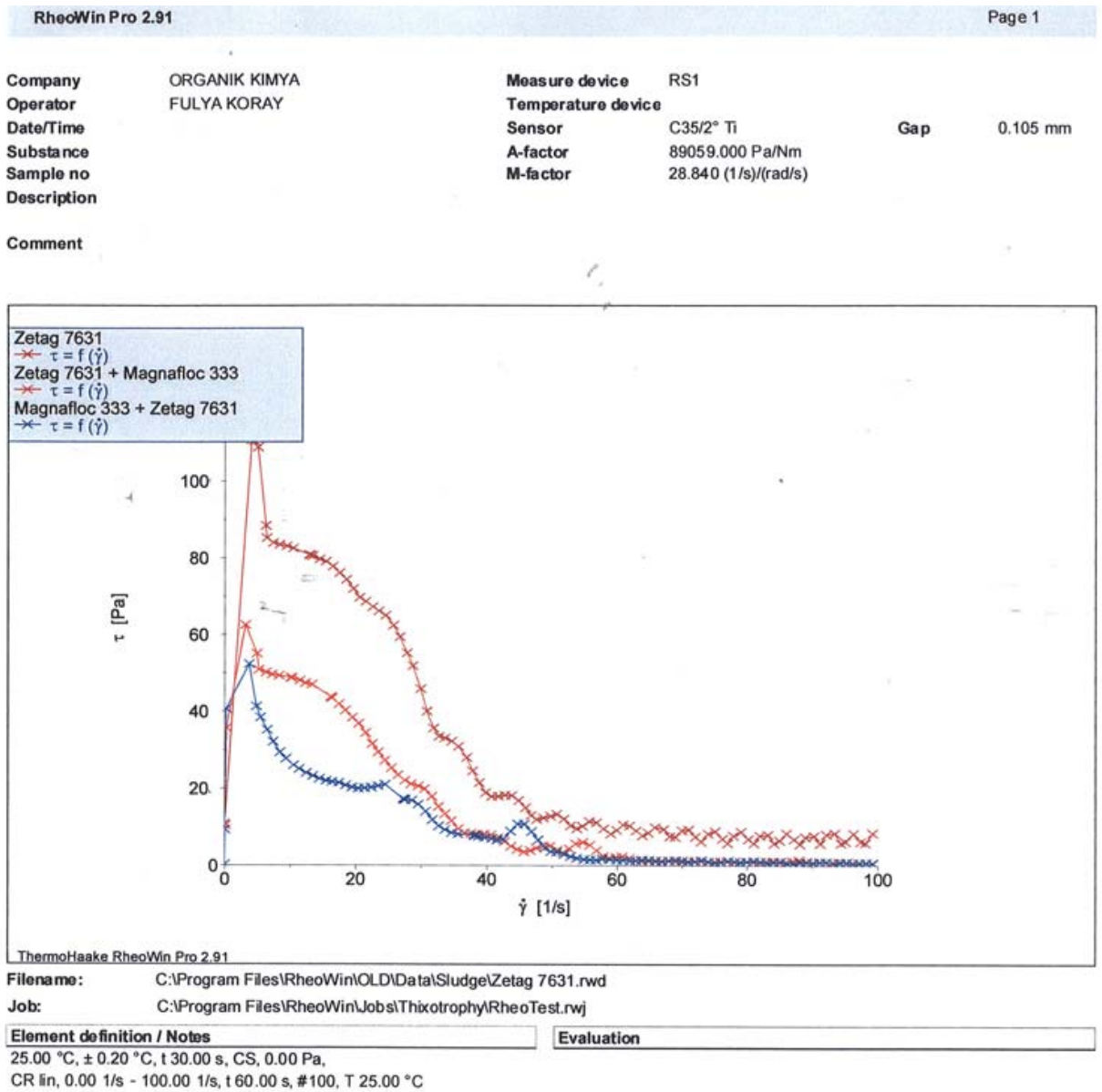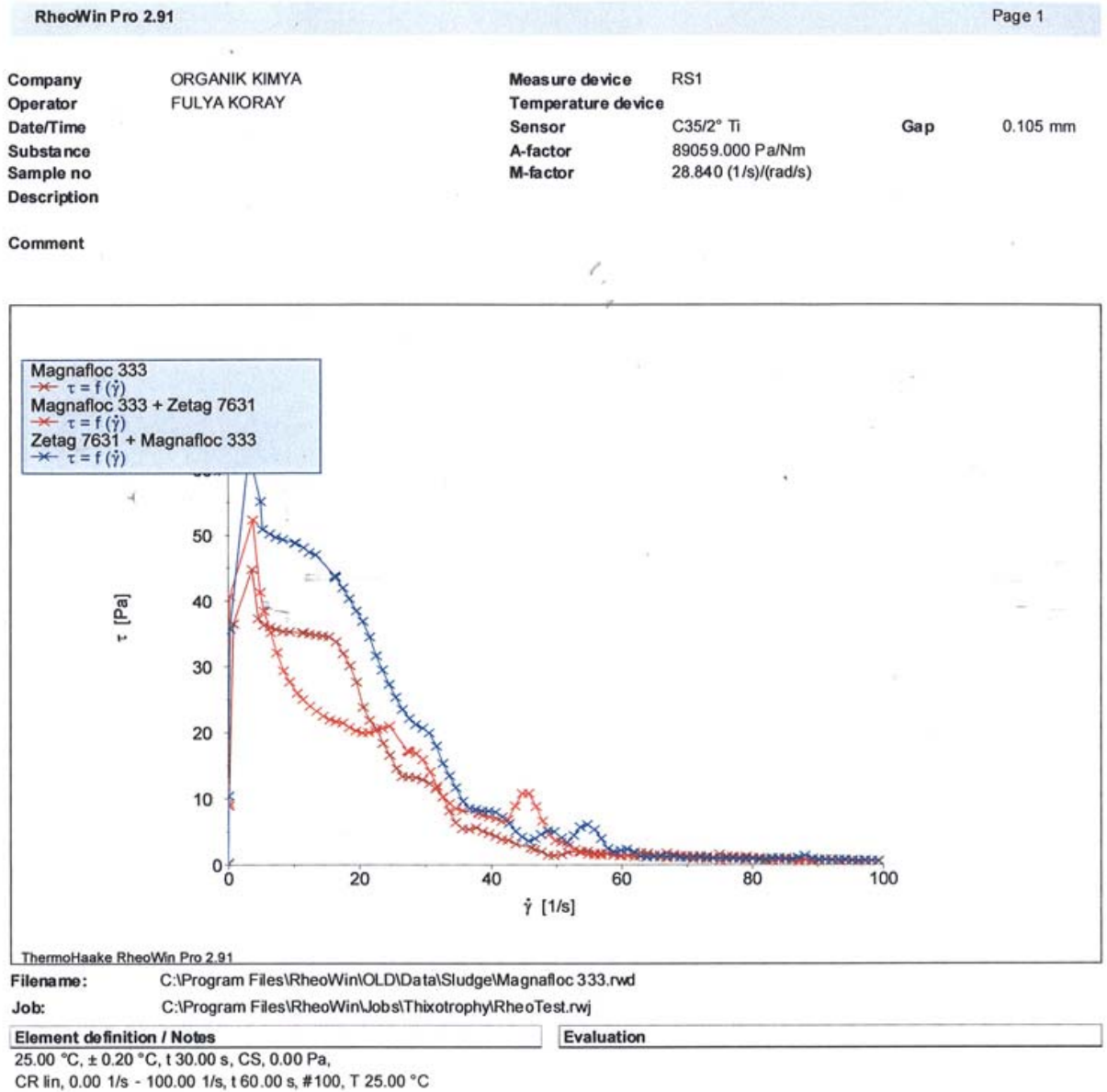Figure 4.33. Rheogram for dual conditioned sludge with Magnafloc 342 (anionic) + Magnafloc 333 (nonionic).

Figure 4.34. Rheogram for dual conditioned sludge with Zetag 7631 (cationic) + Magnafloc 342 (anionic).

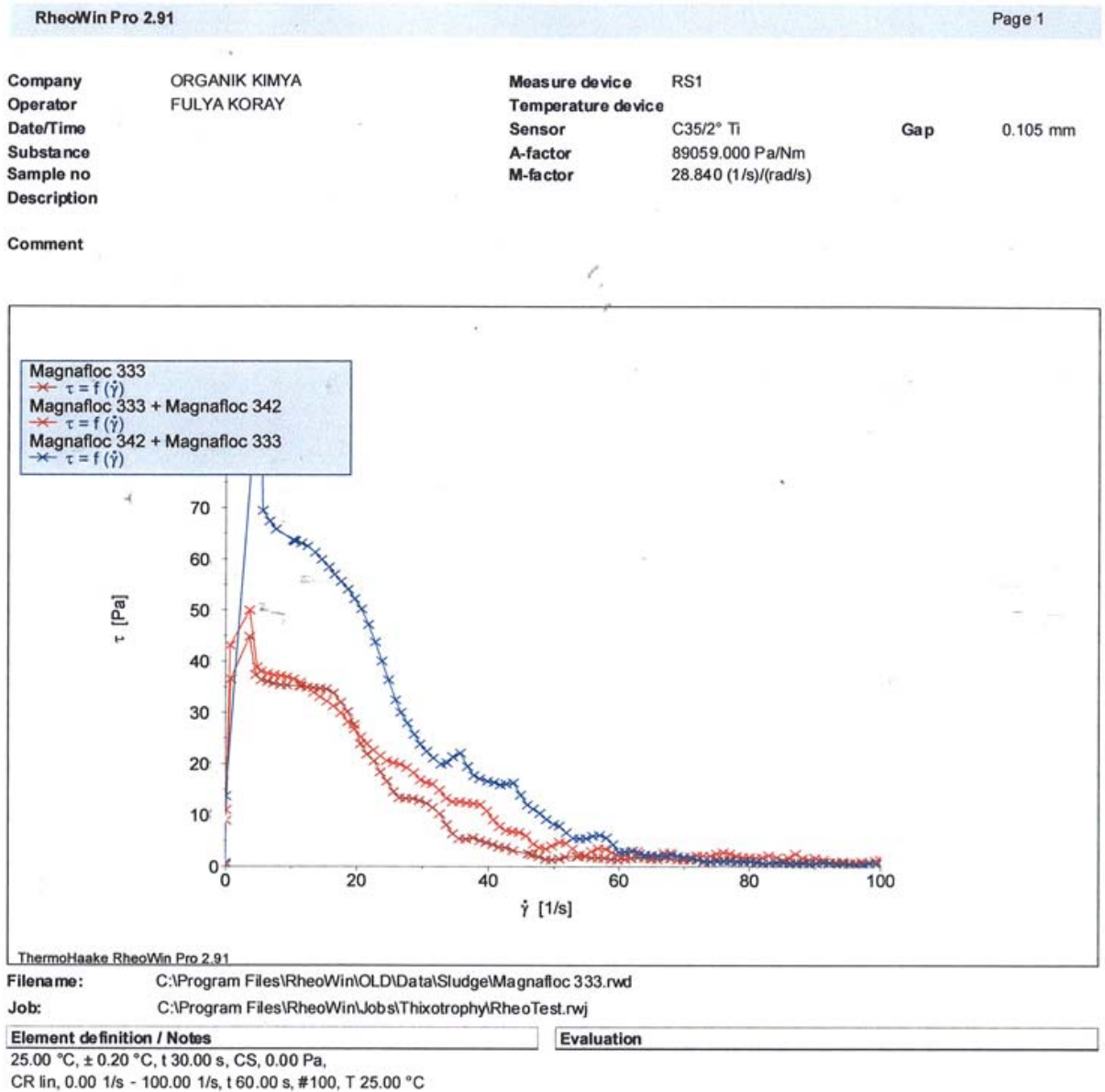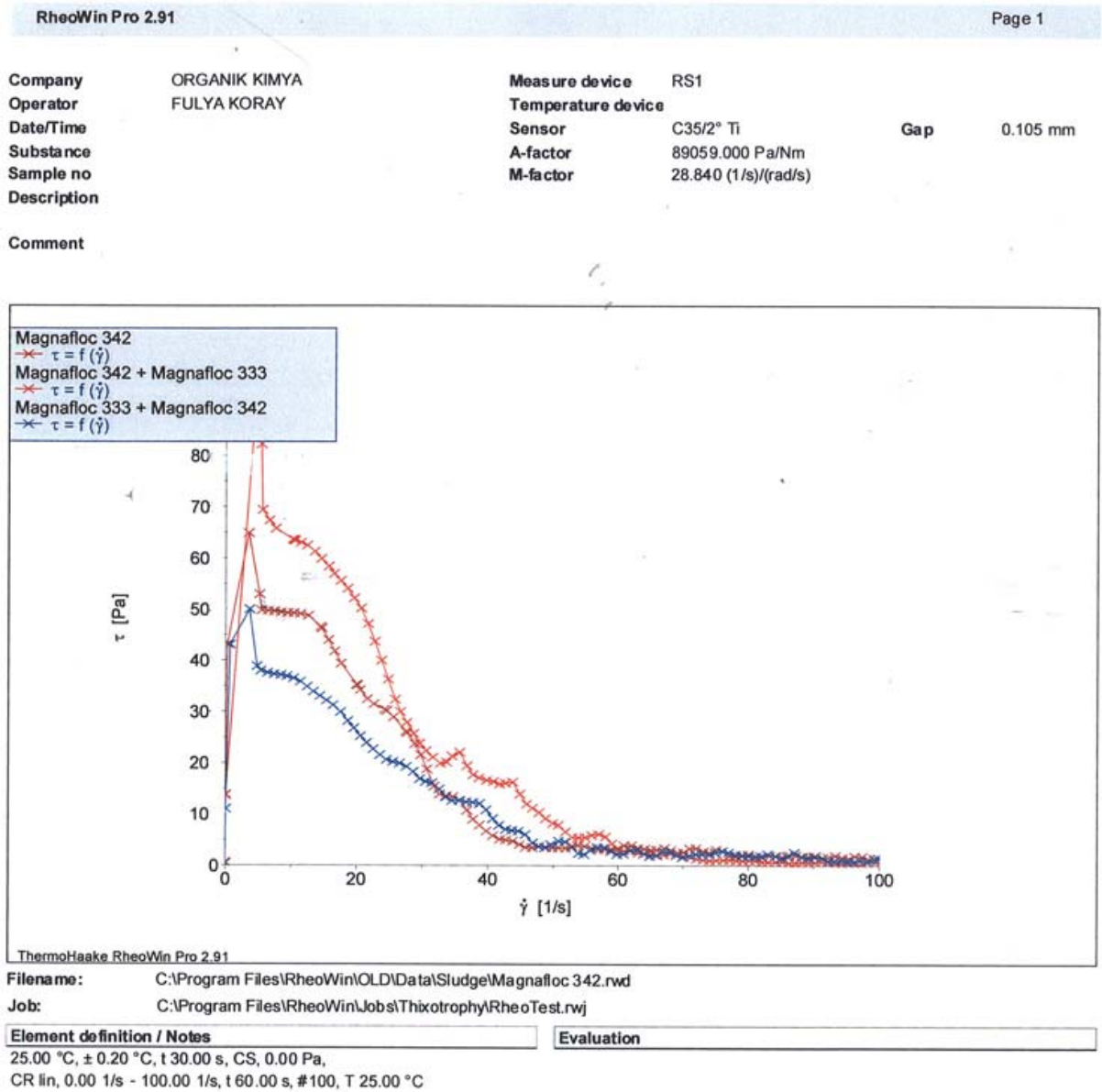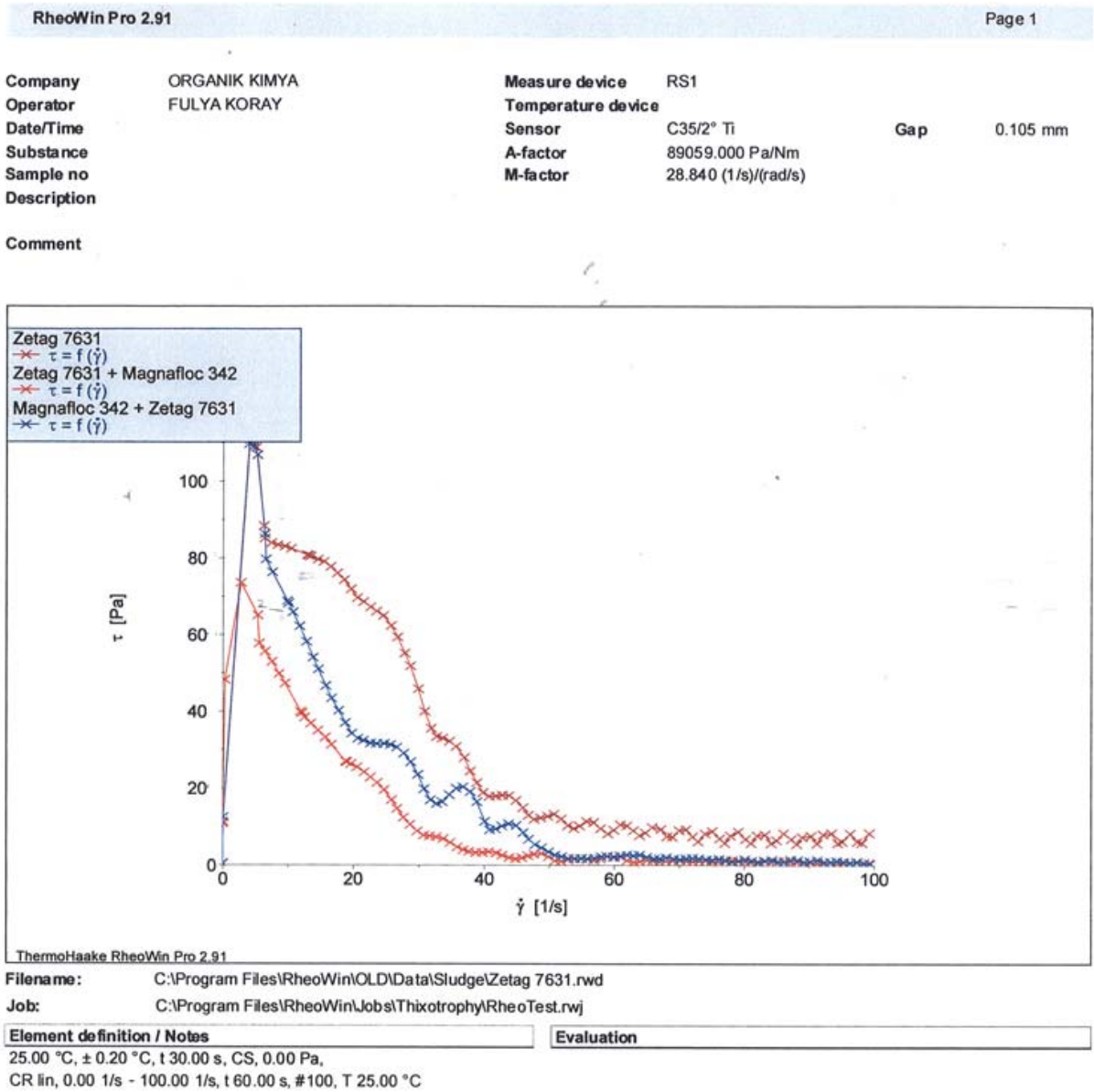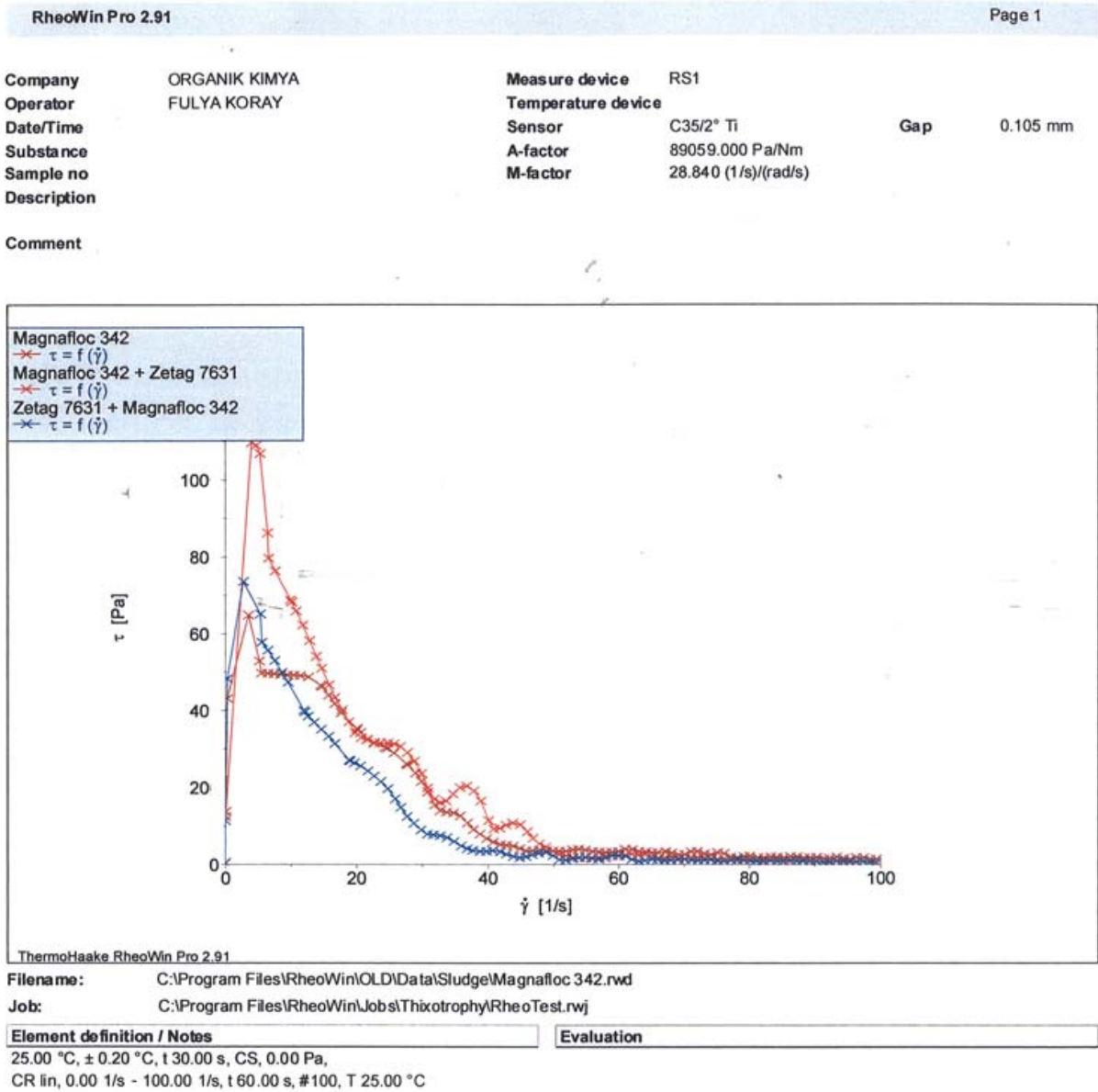Figure 4.35. Rheogram for dual conditioned sludge with Magnafloc 342 (anionic) + Zetag 7631 (cationic).

CONCLUSIONS

This study investigated the effect of dual conditioning on sludge dewaterability and the rheological behavior of the conditioned alum sludges. Based on the results of this study the following conclusions can be drawn.

- Dual conditioning leads to an improvement in the dewaterability of sludges.

- In dual conditioning, the best sludge dewaterability was obtained by adding anionic polymer first and cationic second. When the anionic polymer was added first due to the fact that both groups had the same charge, floc structures were not too strong. After adding the cationic polymer on anionic polymer, charge neutralization was obtained at the optimum level, the best dewaterability was achieved.

- In dual conditioning, the dewaterability of the sludge sample preconditioned with cationic polymer followed by nonionic polymer was better than the sludge sample preconditioned with nonionic polymer followed by cationic polymer.

- When the sludge conditioned with cationic polymer first, the cationic polymer was adsorbed on the sludge particle, and led to the formation of more compact and fragile flocs. After the consequent addition of nonionic polymer, flocs became larger and stronger leading to an increase in sludge dewaterability.

- In dual conditioning of sludges, better dewatering properties were achieved using less amount of polymer than used in single conditioning.

- In the single conditioning, anionic and nonionic polymers were not usually effective, cationic polymers were very effective at the low polymer dosages, depending on the turbidity of the sludge. Cationic polymer formed more compact and stronger flocs as supported by visual and rheological data, and caused the decrease in the sludge dewaterability.

- Based on the rheological data, cationic polymers were added into the sludge sample, the highest shear stress was obtained. The higher shear stress value of the conditioned samples showed that stronger floc formation, resulting in the poor dewaterability due to the rapid clogging properties.

- In dual conditioning, the shear stress values of the sludge samples conditioned with cationic+anionic and cationic+nonionic were lower than the single conditioning of cationic polymer. This showed that the shear stress value in dual conditioning decreased as the cationic polymer dosage decreased. This situation resulted in the improving dewaterability by decreasing the clogging property of the cationic polymer.

- The conditioned sludge samples showed the pseudo-plastic behavior as supported by the rheograms.

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