FLOCCULATION BEHAVIOR OF TWO DIFFERENT CLAY SAMPLES FROM KIRKA TINCAL DEPOSIT

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ABSTRACT

FLOCCULATION BEHAVIOR OF TWO DIFFERENT CLAY SAMPLES FROM KIRKA TINCAL DEPOSIT

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Kırka Boron Plant in Eskişehir region has been producing tincal contentrate and boron products since 1972. Depending on the industrial demand for boron products, the plant capacity has been gradually enlarged by reaching over 1.5 million metric tons per year. This increase in the capacity has caused serious tailings disposal problems. In addition to the great amount of the tailings (400.000 ton solid waste per year), the tailing material contains mostly clay minerals that show colloidal character. Their suspensions are very stable in water and cause flocculation difficulties resulting in very high liquid/solid ratio and complications in management of the plant tailings.

To identify flocculation characteristics of the most abundant minerals (montmorillonite and dolomite) in the tailings, two different clay samples were taken from the Kırka Tincal Mine. XRF analyses were done for elemental composition and XRD analyses were carried out to identify mineralogy of the clay samples. For advanced mineralogical analysis, the oriented clay samples were prepared and subjected to ethylene glycolation and heat treatment. According to the XRF and XRD results, green clay sample is rich in montmorillonite and represents silicate-rich tailings material whereas white clay sample is rich in dolomite and represents dolomitic tailings.

To mimic the actual tailings environment, the green clay and white clay samples were added into borax solutions that buffer pH to 9.40 for the purpose of carrying out controlled experiments. In search of finding alternative ways, the clay suspensions were tried to be flocculated by using new UMA (Unique Molecular Architecture) Magnafloc macropolymers. The flocculation behavior of both green clay and white clay samples was tried to be identified in distilled water and although the very high polymer consumption (up to 2kg/ton) was introduced to the system, the complete flocculation could not be achieved by one stage polymer addition. So, the turbidity of the first stage flocculation were decanted to another beaker and treated with polyethylene oxide at this second stage. As a result, both clays were flocculated by applying two-staged flocculation, respectively UMA Magnafloc and Polyethylene Oxide.

Effects of borax concentration, solid/liquid ratio of simulated pulps, pH of solution and cations (calcium and magnesium) on UMA Magnafloc flocculation were also studied in the scope of this thesis. Flocculation was enhanced by increasing borax concentration, lowering solid/liquid ratio, adjusting pH to 7.00 (although requires great amount of acid due to borax buffer effect) and also adding calcium (up to 500 mg/L) into solution. Addition of Mg^{++} ions into suspensions deteriorated the flocculation of the dolomite-rich white clay and slightly improved the flocculation of the montmorillonite-rich green clay. Furthermore, aging (24 hour) of clay samples also deteriorated flocculation of dolomite-rich clay but it made montmorillonite-rich clay flocculation easier.

Then, ATR-FTIR studies were carried out to analyze the changes on clay surfaces. Ca^{++} and Mg^{++} addition into the suspensions increased the adsorbed water on both clay surfaces and increased the isolated – OH groups depending on this enhanced water-clay surface interaction. According to the infrared results, it was verified that the polymers attached themselves on mineral surfaces through those isolated – OH groups by using hydrogen bonding mechanism.

Keywords: Flocculation,UMA Magnafloc, PEO, turbidity, clay mineralogy, ATR-FTIR, Kırka, tincal, borax, clay.

ÖZ

KIRKA TİNKAL CEVHER YATAĞINDAN ALINAN İKİ FARKLI KİL ÖRNEĞİNİN FLOKÜLASYON DAVRANIŞLARI

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Eylül 2010, 113 sayfa

Eskişehir bölgesinde bulunan Kırka Bor Tesisi 1972 yılından beri tinkal konsantresi ve çeşitli bor türevleri üretmektedir. Bor ürünlerine olan endüstriyel talebin artması dolayısıyla tesis kapasitesi kademeli olarak artırılarak günümüzde 1.5 milyon tona ulaşmıştır. Fakat bu kapasite artışı tesis atıklarının da (yıllık 400.000 ton katı atık) ciddi ölçüde artmasına sebep olmuştur. Buna ek olarak tesis atıkları çoğunlukla kil mineralleri içermektedir ve bu kil mineralleri koloidal karakterde olup su içerisinde uzun süre askıda kalmaktadır. Killerin bu karakteristikleri flokülasyon aşamasında güçlüklere sebep olmakta ve bu durum atıkların düşük katı/sıvı orana sahip olmasına yol açarak tesis atıklarının yönetimini zorlaştırmaktadır.

Tesis atıklarında en çok bulunan minerallerin (montmorillonite ve dolomite) flokülasyon karakterlerinin belirlenebilmesi için Kırka Tinkal Madeninden iki farklı kil örneği alınmıştır. Bu killerin elementel içeriklerinin belirlenebilmesi için XRF analizi ve mineralojik karakterlerinin belirlenebilmesi için XRD analizleri

yapılmıştır. Detay analizler için ise kil örnekleri bazal yüzeyleri üst üste gelecek şekilde (yönlendirilmemiş örnek) tabakalanması sağlanarak etilen glikol ve ısıl işlemlerden geçirilmiştir. XRF ve XRD sonuçlarına göre yeşil kil örneği montmorillonitçe zengindir ve silikat içerikli atık malzemeyi temsil etmektedir; beyaz kil örneği ise dolomitçe zengindir ve karbonat içerikli atık malzemeyi temsil etmektedir.

Kontrollü deneyler yapabilmek için yeşil ve beyaz killer boraks çözeltisine pH = 9.40 değerinde bir tampon bölge oluşturması amaçlanarak eklenmiş ve tesis atıklarının koşulları laboratuar ortamında yaratılmaya çalışılmıştır. Simüle edilen bu pülpler UMA (Unique Molecular Architecture) Magnafloc makropolimerlerinin yardımıyla floküle edilmeye çalışılmış ve killerin çökelme problemi için alternatif bir çözüm yolu aranmıştır. Her iki kilin flokülasyon davranışları incelenmiş ve çok yüksek polimer dozajlarının (2 kg/ton) tatbik edilmesine rağmen tek aşamada (birinci aşama) UMA Magnafloc ile uygulanan flokülasyon tam olarak başarılı olmamıştır. Bu yüzden bu aşamaya ek olarak çöktürülemeyen bulanık kısım başka bir dereceli kaba aktarılarak (ikinci aşama) bu kapta farklı bir flokülant olan PEO ile çöktürülmeye çalışılmıştır. Sonuç olarak, polimerlerin çift aşamada (sırası ile UMA Magnafloc ve PEO) eklenmesi ile killer floküle edilebilmiştir.

Bu tez kapsamında, boraks konsantrasyonunun, katı/sıvı oranının, pülp pH' ının ve kalsiyum ve magnezyum iyonlarının killerin UMA Magnafloc ile flokülasyonuna etkileri ayrıca incelenmiştir. Boraks konsantrasyonunun artırılması, katı sıvı oranının düşürülmesi , pH' ın 7' ye ayarlanmasının (boraksın pH değerinde tampon bölge oluşturmasından dolayı çok yüksek asit tüketimine yol açmasına rağmen) ve kalsiyum (500mg/L değerine varan) eklenmesi ile flokülasyon prosesinin değişen oranlarda iyileşmelere yol açtığı gözlemlenmiştir. Mg iyonu ayrıca test edilmiş fakat özellikle dolomitçe zengin beyaz kil flokülasyonunu zorlaştırdığı ve kalsiyum ile birlikte eklendiğinde de kalsiyumun pozitif etkisinde azalmaya sebep olduğu ortaya çıkmıştır. Buna ek olarak, killerin suda (24 saat) bekletilmesi de dolomitçe zengin killerin flokülasyonunu güçleştirirken silikatça zengin yeşil killerde tam tersi bir etki yaratarak bu killerin çökelmelerini kolaylaştırmıştır.

Kil minerallerinin kalsiyum, magnezyum iyonlarından ve polimerden kaynaklanan yüzey değişiklikleri ATR-FTIR analizleri yapılarak tespit edilmeye çalışılmıştır. Katyonların yüzeyde adsorplanmış su miktarını artırdıkları ve bu etkileşime bağlı olarak yüzeydeki serbest haldeki – OH gruplarının da artmasına sebep olduğu kanıtlanmıştır. Bu ATR-FTIR sonuçlarına göre polimerlerin mineral yüzeylerine bu serbest – OH grupları vasıtası ile hidrojen bağları oluşturarak tutundukları düşünülmektedir.

Anahtar Kelimler: Flokülasyon, UMA Magnafloc, PEO, kil mineralojisi, Kırka, tinkal, boraks, kil.

To My Family

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TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

1.1. Statement of the Problem

Tincal ore in Kırka – Eskişehir region is the largest ore deposit in the world (Garrett, 1998). The first tincal shipment was done in 1972. Then, a tincal production plant was constructed and it was started to produce boron products in 1974. The processing plant was subjected to many rehabilitation works in 1980s and 1990s. These rehabilitation works increased the production capacity gradually due to industrial demand (Garrett, 1998). Nowadays, Kırka tincal concentrator produces over 1.5 million metric tons of tincal concentrate and borax derivatives per year (Lyday, 1996). However, increase in production leads to a substantial amount of solid waste. The Kırka Boron Plant discharges 400.000 ton solid waste each year to produce boron. 250.000 ton solid waste comes from the tincal concentrator and 150.000 ton from the boron derivatives plant (Sabah and Yeşilkaya, 2000). In 1995, the total solid amount in the tailing ponds was calculated as four million tons (Yayık et al., 1995). The amount of solid waste increases continually and causes serious problems in terms of the need for additional tailing ponds, instabilities of the tailing ponds dam due to high liquid/solid ratio of the waste, limited plant layout for discharged material. Such problems lead to a point that the amount of tailings threatens continuous production of the plant.

1.2. Objective and Scope of Thesis

The objective of this study was to characterize flocculation behavior of two different problematic clay type gangue materials that lead to the tailings problem of Kırka tincal concentrator. Prior to the flocculation studies, chemical compositions, mineralogical constituents and surface properties of the clay samples were analyzed in detail. Then, the flocculation experiments of the clay suspensions were carried out with new UMA Magnafloc type flocculant and some conventional flocculants such as polyethylene oxide and polyacrylamides. In the light of the material analyses, flocculation behavior of the clay suspensions was tried to be explained.

The scope of this thesis covers:

I. Detailed mineralogical analysis of the clay samples.
II. Flocculation behavior of colloidal clays with new UMA Magnafloc and conventional polyethylene oxide.
III. Effect of borax concentration on the flocculation.
IV. Effect of solid / liquid ratio on the flocculation.
V. Effect calcium and magnesium ions on the flocculation.
VI. Behavioral change in the flocculation after clay samples subjected to aging in water.
VII. Comparison of several flocculant performances with new UMA Magnafloc polymer.
VIII. ATR FT-IR studies to identify surface properties of clays before and after calcium, magnesium and polymer addition.

CHAPTER 2

LITERATURE SURVEY

2.1 Flocculation

Dewatering is a process identified as a part of solid-liquid separation and its aim is simply to reduce the moisture content of filter cakes or sediments. The most widely used ways of achieving this are mechanical compression of cakes, air displacement under vacuum or pressure and drainage in a gravitational or centrifugal system. All of these methods and related equipment are used in mineral processing and hydrometallurgical plants individually or combined with each other in similar ways. This dewatering procedure applied in the plant flow sheet is performed by the vibrating screens, DSM, Sweco, hydrocyclone, mechanical classifier, thickener and filter (Garrett, 1998). When products of these equipment are considered, it can be seen that the solid-liquid separation is never complete, but it can be improved with the addition of dewatering aids (Svalovsky, 2000). The flocculants help to the dewatering equipment and accelerate dewatering and improve solid-liquid ratio.

The purpose of flocculation is to form aggregates or flocs from finely dispersed particles with the help of natural and synthetic polymeric substances which are referred to as flocculants. Flocculation has been commonly applied for domestic and industrial wastewater treatments for solid/liquid separation. To achieve sufficient separation, many different types of flocculants are used according to waste material type and surrounding conditions because flocculation processes are very sensitive to the surface phenomena, solid-liquid or solid-polymer interaction, environmental factors, pulp (or solution) content which can hinder the sedimentation or accelerate the process, presence of counter ions and simili-ions, mineralogy and particle size, amount of adsorption of the polymer on particle surface and even the porosity. Each of them determines the flocculation rate and efficiency. So, determination of the flocculation behavior of the suspensions is very important for an efficient solid/liquid separation.

2.2 Mechanism of Flocculation

Polymeric flocculation process has several mechanisms. But most important mechanisms of flocculation by polyelectrolytes were considered to involve two processes of surface charge neutralization and bridging (Lu et al., 2005). Moreover, van der Waals attraction and osmotic pressure may be considered as auxiliary factors additional to those. Charge neutralization and bridging mechanisms will be explained in the following sections.

2.2.1 Charge-Patch Neutralization Mechanism

Charge-patch neutralization mechanism was proposed by Gregory (1973). The solid material surface charge in the pulp is determined and flocculation reagent type is decided according to this. The opposite of the solid material surface charge is selected for flocculant charge type. Gregory’s (1973) theory explains specially that if the flocculated material has negative surface charge, the flocculant should have high positive surface charge for the electrostatic attraction, and low to moderate molecular weight to form patches on the particle surface. Under these circumstances, the charged polymer is visualized to be much smaller than the surface area of the particle and forms patch on the surface. As a result of this patch system, the surface charge of particles is neutralized and after collision of particles flocs are formed due to this charge-patch neutralization mechanism. The process of charge neutralization proceeds as shown in Figure 1.

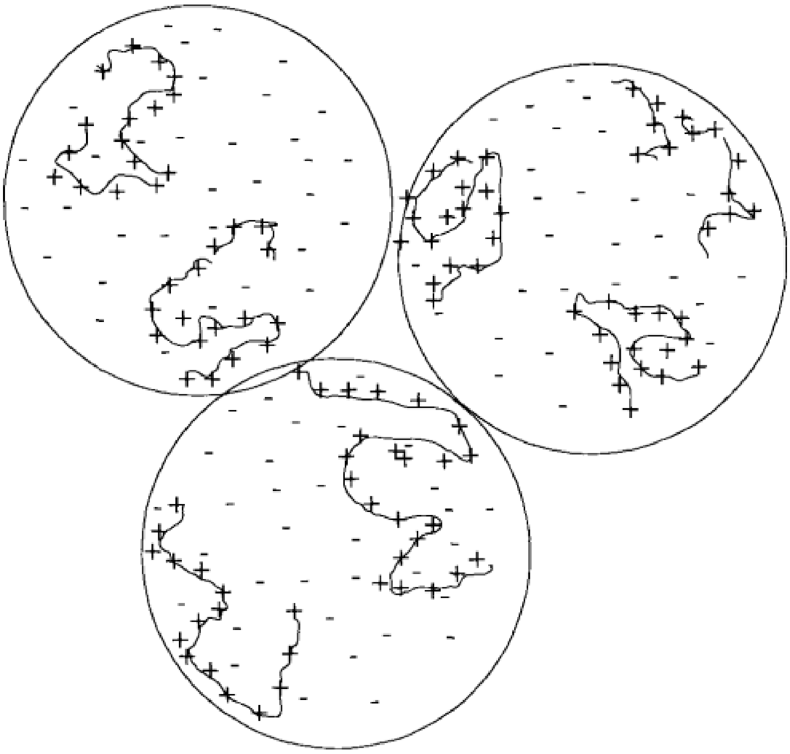


Figure 1. Electrostatic Patch Model of Polymer Adsorption Leading to Flocculation (Lue & Pugh, 2005)

This theory would lead to the consideration that cationic polyelectrolytes would be the most suitable flocculants since most suspensions encountered in the minerals industry contain negatively charged particles. Although this is true for charge neutralization purposes, and attraction of the polymer to the particle surface, it is not necessarily true for the all cases in the minerals industry. Many researchers (Ellis et al., 1979; Luckham & Rossi, 1999; Mpofu et al., 2003; Huang & Dixon, 2000; Farinato et al., 1999; Vucinic et al., 1998) proved that “anionic” high molecular weight polyacrylamide (PAM) was very effective in flocculation of “negatively charged clay particles” such as montmorillonite, and it was claimed that bridging mechanism can dominate charge-patch neutralization mechanism in flocculation processes (Mpofu et al., 2005). So, it was suggested that, if charge neutralization mechanism does not work for specified case, one should consider directly bridging mechanism domination in terms of effective flocculation performance and should choose polymer according to this (Hughes, 2000). For example, Kırka Tincal Processing Plant tailings are flocculated by anionic reagents, but not by cationic ones (Garrett, 1998) even though the surface charge of the tailings particles is negative. The same situation is also pronounced for the Rio Tinto Borax Processing Plant in USA (Garrett, 1998). In conclusion, although the charge neutralization is an important step in flocculation mechanism, especially when cationic flocculants are used; it may be overwhelmed by the “bridging mechanism” in mineral processing industry.

2.2.2 Bridging Mechanism

Bridging is associated with polymers of high molecular weight where the tails and loops of the macromolecule can form links between particles. When a polymeric macromolecule is added at an optimum dosage, it can adsorb on particles through several segments with the other parts of the molecule extending into the solution (Figure 2.a). Flocculation by the bridging mechanism may occur in two ways. Bridging can take places between two particles linked by the long chain of one polymer (Figure 2.b) or the particles can be linked by the chain (Figure 2.c) of polymer molecules separately adsorbed on different particle surfaces.

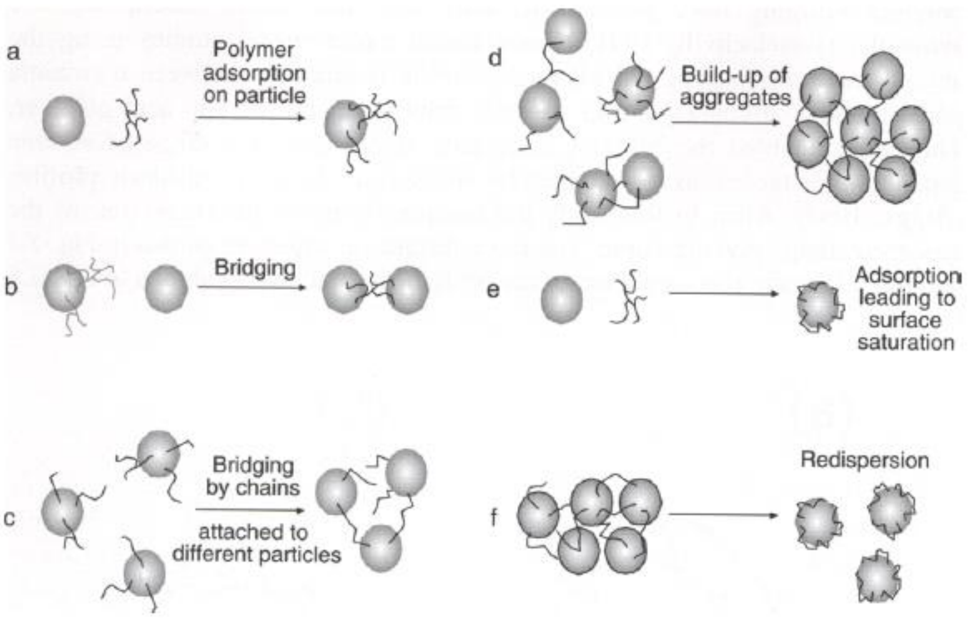


Figure 2. Bridging Mechanism in Flocculation (Lu etal., 2005)

The later situation can occur in the case where the surface coverage of polymer is very high, the loops, tails dangling outwards are long, and the degree of association between polymer chains is strong. By means of these bridging mechanisms, aggregates are built up (Figure 2.d). Bridging can be affected by the pH and the presence of polyvalent counterions influences the polymer uncoiling. An increase in the ionic strength could cause the polymer to coil up and weaken the bridging bonds. Another possibility in flocculation procedure is that the tail of the flocculant can also adsorb on the other active sites of the same particle and as a result, the flocculation fails (Figure 2.e). In such cases the surface may become saturated so that no more adsorbable site is available on the surfaces. This situation causes the dispersion of the particles in solution. This case was also reported by Deng (2006) who used PAM 836A anionic flocculants for negatively charged clay materials. Deng’s studies showed that this type of flocculant cause serious dispersions of clay particles because the surface is saturated with negatively charged PAM 836A like in Figure 2.e and concluded that the PAM836A anionic flocculant is not suitable for flocculation of smectite, illite and kaolinite. In other cases, once the bridging mechanism is even established between many particles, they can be destructed by many external effects, like agitation. After this destruction the particles are re-dispersed as shown in Figure 2.f.

Another aspect of flocculation is the elongation of the polymer from particle surfaces to solution. Some experimental studies were carried out by “Atomic Force Microscope”. Biggs (2005) studied molecular force factor between bridged particles as a function of distance. This enables the bridging and steric interaction at a range of surface separation distances to be studied by measuring the force-distance profiles. In general, it can be said that if the bridged particle distance is greater, the interparticle forces (like van der Waals, electrostatic forces) decreases and compression rate is distorted. It was stated that those forces decreased from Figure 3.A to Figure 3.E (Lu et al., 2005).

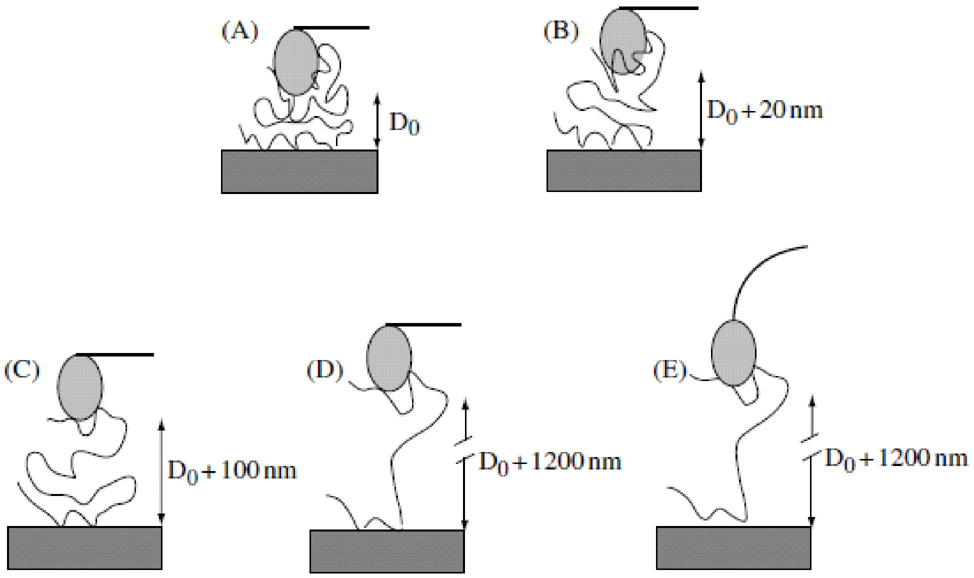


Figure 3. Bridging Interaction at Various Surface Separations (Lu et al., 2005)

To sum up, the followings are essential for effective bridging (Lu et al., 2005):

1. There should be enough sites on the particle surfaces for polymer adsorption.
2. Adsorbed polymer on particle surface can extend chain, loops and tails into solution.

In conclusion, as explained in the Figure 3.A-E, the behavior of the flocculants towards the flocculated material is very important for sedimentation, dewatering or clarification purposes because bridging and surface coverage of polymers on particles define rate of flocculation and efficiency of the process.

2.3 Zeta Potential

Suspended clay particles in an aqueous environment develop an electrical double layer on their surfaces. This double layer phenomenon was generally dependent on the aqurous solution and the particle characteristics. Zeta potential arises at this point and defined as the average potential in the electrical double layer at the zone of shear between a mobile particle and the immobile liquid phase in which a particle suspended. The potential difference and the surface charge of the particles arises from ionization of surface groups, adsorption of surface active materials, permanent charge associated with crystal structure or combination of these mechanism (Ward, 2008). In minerals processing, the zeta potential is a very important issue because it gives clues about the behavior of mineral surface towards several factors, reagent selection for required process, and effect of added reagent on the mineral surface.

Different adsorbates change zeta potential of mineral surfaces in different ways. Cationic and anionic electrolytes affect the zeta potential by means of charge neutralization (or direct change of the surface charge sign). On the other hand, cationic, anionic or non-ionic polyelectrolytes can also change the zeta potential of the mineral surfaces. It was expected that the presence of polymeric flocculants (especially non-ionic polymers) were assumed to induce no effect on surface charge density, charge distribution in diffuse layer and specific adsorption of ions. Nevertheless, a reduction was observed in the absolute value of the zeta potentials of the negatively charged clay particles after polymer (anionic or non-ionic ones) adsorption on the particle surfaces. Moreover, it was found that increasing polymer dosages gradually resulted in the greater charge neutralization of the negatively charged clay surfaces (the zeta potential of the clay particles approaches to 0 mV) and increasing adsorbed polymer layer thickness on the clay surfaces (Mpofu et al., 2003). This was explained that a displacement of the shear plane occurs compared to the position in the absence of adsorbed polymer (Satyanarayana, 2004). The displacement (Figure 4) of shear plane depends on the thickness and the head-tail orientation of the polymers (Lu et al., 2005). Due to the inverse proportion between zeta potential and thickness of double layer, zeta potential value decreases. This phenomenon was concluded that polymeric flocculants can change the zeta potential of particles by increasing the distance of shear plane in addition to the charge patch neutralization mechanism. So, the thickness of the adsorbed polymer layer should be taken into the consideration in the flocculation process.

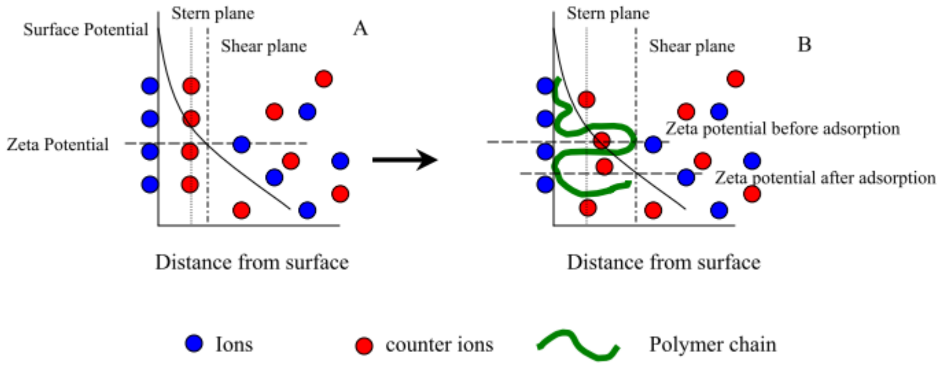


Figure 4. Zeta Potential Change Before and After Polymer Adsorbed on the Surface (El-Midany, 2004)

2.4 Common Industrial Flocculants

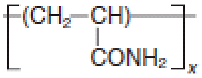
Flocculants are classified depending on physicochemical characteristics (molecular weight and ionic strength) and their origin (natural or synthetic). Synthetic flocculants were reported with many advantages over natural flocculants (Lu et al., 2005) and were used more widely than natural polymers in industrial flocculation processes because they are superior flocculation agents at low dosage, have lower degredation and have a certain molecular weight distribution. Molecular weight of these synthetic polymers depends on their chain length. Longer polymer chains commonly referred to as high molecular weight whereas shorter polymer chains refer to lower molecular weight. Moreover, ionic character of the synthetic flocculants depends on their polar groups that classify polymers into anionic, cationic and nonionic groups. These two factors are very important in terms of the flocculant selection. The most common ones of these synthetics polymers are polyacrylamides and polyethylene oxides because their molecular weight ranges from 7 millions to 20 millions and they can produce firm flocs (Lu et al., 2005). Polyacrylamides and polyethylene oxides will be explained in the following.

In general Polyacrylamide (PAM) based polymers are used and commercially available for the demand of industry. They are generally effective in the flocculation of coarser particles. Nevertheless, the flocculation of the fine size particles with polyacrylamide is challenging and polyacrylamide performance decreases sharply. So, for the purpose of making the fine size particles flocculated, polyethylene oxide (PEO) is commonly used. Bureau of Mines (US) (Scheiner et al., 1985) stated that the fine particles such as phosphate slimes, potash – clay wastes and talc tailings can be flocculated with PEO. It is particularly recommended for the flocculation of the clay tailings. For the stable suspensions, double flocculant system can be used to obtain much denser solid in the flocculation of the tailings. For instance, nonionic polyethylene oxide and anionic polyacrylamide polymeric flocculants mixed and applied in the industry to flocculate such stable suspensions (Taneri, 1988). On the other hand, the polyvinyl alcohol type flocculants may not be suitable for the flocculation of tincal tailings because the boron products especially borates interacts with polyvinyl alcohol to form very viscous slimy gel (Robinson, 1979) which can cause significant boron loss. For this reason, polyvinyl alcohol will not be mentioned in the scope of this thesis but other common industrial polymers such as polyacrylamide, polyethylene oxide and new UMA Magnafloc will be explained in the followings.

2.**4.1 Polyacrylamides**

Polyacrylamides are the most important commercial water soluble polymers. These polymers are used in a wide range of industrial application such as soil erosion control, soil conditioning, irrigation control, oil recovery, industrial and domestic water treatment (Deng et al., 2006). Their general formula is (Hughes, 2000):

Polyacrylamides



$$\left[-(CH_2-\underset{\displaystyle CONH_2}{CH})- \right]_x$$

They have generally molecular weight of 15 million. In extreme cases, the molecular weight of polyacrylamides can be up to 30 million (Somasundaran & Moudgil, 1987). Anionic, cationic and non-ionic types of polyacrylamides are available and anionic and cationic ones have varying charge densities. Cationic polyacrylamides have higher charge than anionic polyacrylamides but the molecular weight of the cationic polymer are lower (< 1 million) and they have not been technologically developed as much as anionic ones (Skuse, 2002). pH is another factor that affects polyacrylamides. Cationic polyacrylamides are very sensitive to pH of environment whereas anionic and nonionic polyacrylamides are less sensitive to pH (especially nonionic flocculants work even at high pH values successfully). At optimum pH, polyacrylamides attach themselves on particle surfaces by forming hydrogen bonds between the amide groups and the active sites of particle surface (Figure 5). For instance, formation of these hydrogen bonds seems to be competitive with hydrogen bond formation between neighboring aluminol and silanol groups of clay minerals. Hydrogen bonding to silanol groups as “anchoring sites” is promoted in acidic medium. On the other hand, bonding to aluminol groups is favored in alkaline medium (Bergaya et. al., 2006).

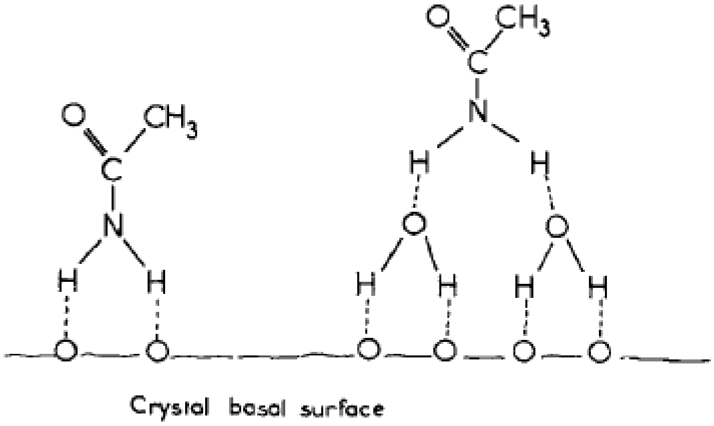


Figure 5. Hydrogen Bonding Mechanism and Polymer Interaction with Basal Surface of Clays (Stutzmann and Siffert, 1977)

In conclusion, Stutzmann and Siffert (1977) made the inference that adsorption of polyacrylamide onto clays in weakly acid medium corresponds to “chemisorptions”. The polarization of the water molecules in contact with the exchangeable cations of the clay generates protons on the edge surface of the clay crystallites. The polymer is adsorbed onto these protonated sites after a transfer of hydrogen to the amide groups has occurred (Stutzmann and Siffert, 1977). Moreover, the interaction between the polyacrylamide and the clay micelles is attended by a co-flocculation characterized by the formation of polymer bridges between several mineral particles. During the co-flocculation, “physical adsorption” can be superimposed on “chemisorptions”.

2.4.2 New Modified Polyacrylamides: UMA Magnaflocs

The mineral processing industry requires great solid-liquid separation ratios due partly to environmental considerations and partly to technical and cost efficiencies in recent years. This situation led to the development of improved, high performance flocculants. Average molecular weight of polymer molecules increased, structure and chemical composition were enhanced for the purpose of dewatering. This trend came out recently with new polymeric type of flocculant called UMA Magnaflocs with the help of the state of art technology in mineral processing and chemistry.

In the literature and the industrial applications of solid-liquid separation, it is well known that the clay particles, especially in ultra-fine size particles, are very difficult to flocculate. In the mineral processing industry, conventional high-molecular-weight polymers are considered as linear structures with two dimensions. These flocculants sometimes do not provide the required solid/liquid separation performance. So, some companies designed polymeric molecular flocculants with unique molecular architecture (UMA) to enhance flocculation process. It is claimed that this technology covers highly branched and interactive polymer chains and produce flocculant solutions containing a proportion of semi-particulate entities and polymer chains reticulated in three dimensions which produce flocs of different characteristics than those formed by conventional flocculants; denser and stronger flocs are produced containing less intrafloccular water (Pearse, 2003). Pearse also claims and illustrates the mechanism difference of two dimensional and three dimensional polymeric flocculants as shown in the Figure 6, Figure 7 and Figure 8.

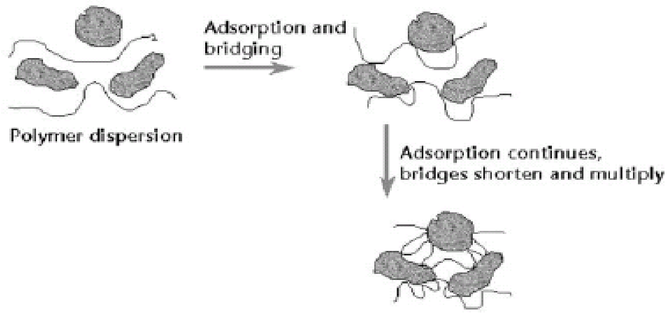


Figure 6. Conventional View of Polymer Bridging in Flocculation (Pearse, 2003)

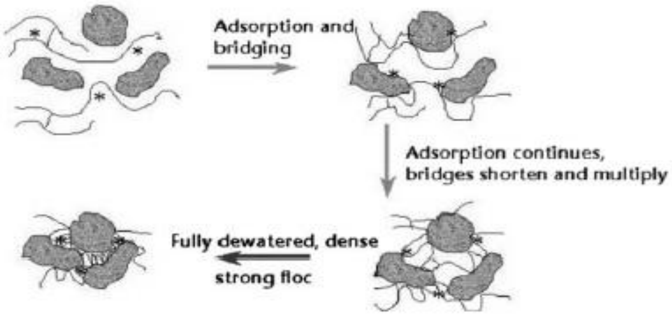


Figure 7. Flocculation with UMA Magnafloc Macro-Polymer (Pearse, 2003)

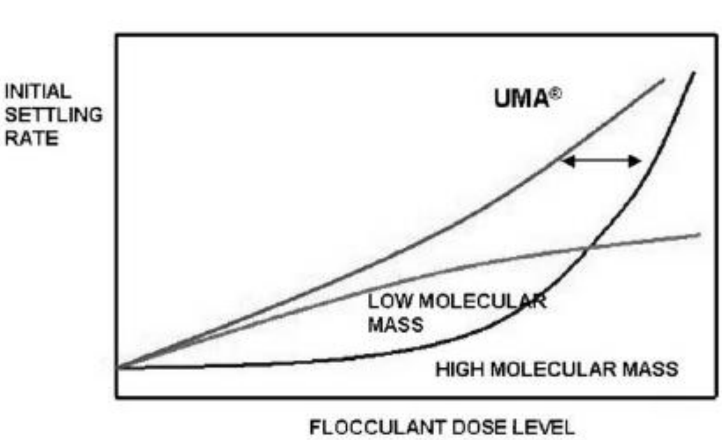


Figure 8. Comparison of Conventional Polymers and UMA Magnafloc

This mechanism shown in Figure 7 proved as valid and effective for especially clay material and the laboratory works showed that the increasing polymer dosage of UMA flocculants lead to the increasing settling rate (Cengiz et al., 2009) in contrast to some anionic polyacrylamide (Deng et al., 2006), like PAM836A. This means that some anionic polymers (PAM836A) adsorbed at great level and cause the clay material repulse each other that form much more stable colloidal dispersion. Nevertheless, the researchers (Pearse et al., 2001) have made comparative studies to evaluate flocculation efficiency of UMA polymeric flocculants and they summarized graphically the performance behavior of UMA polymers and conventional polymers as shown in Figure 8.

Studies on UMA Magnafloc flocculants' adsorption mechanism proved that the active groups of this polymer are functional within the pH range of 4-10 (Cengiz et al., 2009). Another study (Cengiz et al., 2004) showed that the most efficient pH for clay tailings flocculation was around neutral pH. This was explained with the following mechanism: when suspension pH increases, the anionicity of the macromolecules increases; however the surface of the particles becomes more negatively charged and a repulsion force naturally occurs between the polymer particles and clay particles (Cengiz et al., 2004). This repulsion may decrease flocculation efficiency.

According to some researchers (Pearse et al., 2001; Cengiz et al., 2004) and the company authorities, this phenomenon concludes in better overall dosage efficiency, better clarification at best settling rate and better sediment volume for clay material than conventional flocculants. In addition, it was proved that UMA polymers were stable toward the agitation of the suspensions.

2.4.3 Polyethylene Oxides

Polyethylene oxide PEO is a commercial polymer which has been successfully used as flocculant for clays (Mathur and Moudgil, 1997) since 1980s

(Somasundaran and Hubbard, 2004). PEO is also used for the flocculation of ultra-fine silica particles. PEO is water soluble nonionic polymer with the following generalized formula (Hughes, 2000):

Polyethylenoxide $$\left[(O-CH_2-CH_2) \right]_x$$

It is commercially available with a wide range of molecular weight. According to well known polymer producer Sigma-Aldrich, polyethylene glycol (PEG), polyoxyethylene and polyethylene oxide (PEO) have similar meaning with some differences. They are all synthetic polyether that is readily available in a range of molecular weights. Usually, polymers with molecular weight less than 100 000 are called as polyethylene glycols and greater molecular weight polymer called as polyethylene oxides (Sigma Aldrich Company, 2009; Theng, 1979). The molecular weight of polyethylene oxides used in minerals industry shows variations between 5 million and 10 million (Somasundaran and Hubbard, 2004). Unlike polyacrylamides, polyethylene oxides are only available as nonionic polymers. This nonionic character makes polyethylene oxides insensitive to anionic species in suspensions according to Somasundaran and Hubbard (2004). Mpofu et al. (2003) also claim that the nonionic character makes polyethyelene oxide chain durable against mechanical mixing. So, polyethylene oxide macromolecules produce strong and dense flocs under moderate to high shear rates. Adsorption behavior of PEO on oxides was stated by several writers (Lu et al., 2005; Mathur and Moudgil, 1997; McFarlene et al., 2008). Mineral and polyethylene oxide interaction was believed to be through a hydrogen bonding mechanism involving the isolated surface hydroxyls of mineral surfaces and the ether oxygen of the polyethylene oxide polymer molecule (Mathur and Moudgil, 1997) which can be seen in Figure 9.

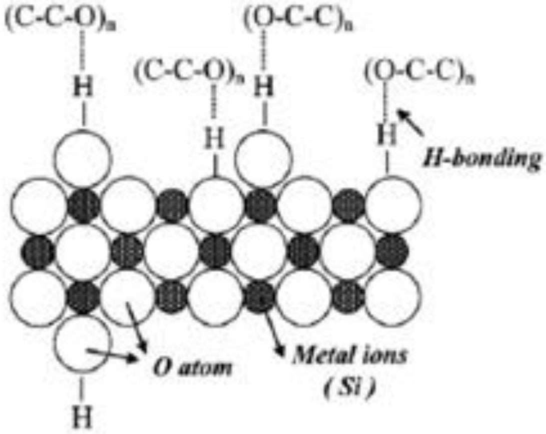


Figure 9. Polyethylene Oxide Interaction with Mineral Surfaces (Su & Shen, 2008)

Hydrogen bonding is assumed to be a ubiquitous mechanism of the polymer adsorption on hydrophilic surfaces but polyethylene oxides could not be adsorbed on the surface of some metal oxides. Although varying range of polyethylene oxides were tested with TiO_2, Fe_2O_3, Al_2O_3, SiO_2 and MgO only the SiO_2 was flocculated and other oxides showed no adsorption and flocculation (Mathur and Moudgil, 1997). The systems that could not flocculate with polyethylene oxide were suggested to be treated with $CaCl_2$ prior to flocculant addition. $CaCl_2$ treated suspensions easily flocculated with polyethylene oxide and this was explained with polyethylene oxides segments attached on Ca^{++} adsorbed sites on particle surfaces (due to high affinity of polyethylene oxides to calcium) by leaving polymer loops and tails available for bridging adjacent particles (Somasundaran and Hubbard, 2004). In conclusion, polyethylene oxide has greater particle interactions more strongly networked flocs and shows higher resistance to shear compared to polyacrylamides at the same dosages (Mpofu et al., 2005). Polyethylene oxide also proved to be more favorable than polyacrylamides especially in the flocculation of clay suspensions.

2.5 Specific Studies on the Flocculation of Dolomite and Montmorillonite Minerals

2.5.1 Flocculation of Dolomite

Dolomite flocculation and sedimentation behavior changes from one sample to another although the chemical formulas and the analysis are the same. For example one would think that dolomite could be more easily flocculated than clay minerals but, this is not the case; Gür et al. (1996) showed that montmorillonite is more easily flocculated than dolomite although they used different polyelectrolytes for sedimentation. This proves that some other mechanisms stemmed from the dolomite itself are involved in the flocculation process. In 1993, Moudgil and Behl studied the flocculation mechanism of many different dolomite samples from various geologic formations. Each sample's mineralogical properties, surface chemistry, dissolution characteristic in water, polymer adsorption properties were studied by them. Moudgil and Behl (1993) concluded that dolomite samples of similar chemical composition but different surface chemical properties behaved differently even with the same polymeric flocculants. Six dolomite samples were tested for sedimentation by polymer addition but only four of them can be flocculated and just one of them flocculated at an amount of 98%. Two of them (samples including 100% dolomite mineral) are non-flocculated and no sedimentation occurs up to 5kg / t polymer used during the experiments. Moudgil and Behl (1993) could not explain the variation in the flocculation behavior of the dolomite samples. In 1997, Mathur and Moudgil tried to explain this problem in dolomite flocculation. They claimed that the IR-bands attributed to free hydroxyls on dolomite were actually those of a clay coating present on the dolomite samples and they thought that the flocculant adsorbed on the clay coatings on the dolomite instead of the dolomite itself. In conclusion, the natural clay coating on dolomite surfaces seems responsible from the flocculation of dolomite suspensions.

Dolomite is a very problematic mineral not only in minerals engineering but also in soil science. Dolomite-rich soils were subjected to rapid dispersion in aquatic solutions. Dolomite mineral in soil formations introduces Ca and Mg into the solution and they are adsorbed on the cation exchange sites of the soil particle's surface. However, Mg released from dolomite is believed to be the source of this dispersion because hydration radius of Mg ion is greater due to its higher hydration energy (Pansu and Gautheyrou, 2006) than Ca ion. The greater hydration radius of Mg ion causes larger separation distance between clay layers and less attraction between them by preventing flocculation. As a result of this, dolomite mineral presence in the soil formations seems to be responsible from severe erosion during rainfalls due to this dispersive character (Dontsova and Norton, 1999). In addition to this, Donstova and Norton (1999) stated that the dispersive characteristic of Mg ions may deteriorate flocculation (or coagulation) of clay suspensions.

2.5.2 Flocculation of Montmorillonite

Montmorillonite is a swelling type clay mineral in smectite group. Clay minerals such as kaolin and smectite group clay minerals are commonly present in the tailings of minerals industry. Their presence can cause very difficult dewatering and handling problems in terms of gelation and space filling "card house" structures which result in high yield stress, high flocculant demand, low settling rates and poor supernatant clarity (Addai-Mensah, 2007). Montmorillonite-rich clays can be thickened and dewatered with high molecular weight flocculants with the help of the hydrolyzable metal ions leading to high settling rates from 10 to 30 m/h and acceptable supernatant clarity less than 50 mg/dm^3 suspended solids (Mpofu et al., 2005).

Moreover, swelling property of the montmorillonite can make the thickening difficult. Smectite group clay minerals containing monovalent cations (Na, Li, and Mg) may cause osmotic swelling with higher water uptake causing the interlayer spacing to increase up to 30-40 Å. This situation result in high yield stress which presents difficulties to the flocculation process of clay suspensions. Flocculation behavior of montmorillonite type clay suspensions is very sensitive to the pulp environment: hardness of water, presence of cations, pH. The most important ones of these parameters in the flocculation of the montmorillonite suspensions are the amount of Ca ions and pH (Mpofu et al., 2005; Addai-Mensah, 2007) because the degree of swelling and indirectly the high yield stress can be controlled by pH and multivalent cations addition, Ca(II), Al(III) (McFarlene et al., 2008).

Another important point in the flocculation studies of montmorillonite suspensions is the polymer consumption. In parallelism with the industry, most of laboratory studies do not exceed the addition of 1500 g flocculant per ton solids (Addai-Mensah, 2007). In the flocculation of montmorillonite suspensions, the reagent consumption is relatively high due to very high surface area of this mineral. The polymer consumptions of montmorillonite suspensions were reported by Addai-Mensah (2007) in a comparative study that polyacrylamides flocculated the montmorillonite suspensions with a dosage of 1000 gram per ton solid whereas polyethylene oxide did with a dosage of 600 gram per ton solid (Addai-Mensah, 2007). The polymer consumptions in the flocculation of montmorillonite-rich suspensions were very high so to stay within the economical limit flocculants are generally assisted by electrolytes.

Recently, severe agitation conditions (up to 4000 rpm) were applied to flocculation process (Maes et al., 2003) resulting in good mixture of high molecular weight polymeric flocculants with montmorillonite particles by increasing the probability of particle – polymer collision. This method is called “Ultra-Flocculation” and especially studied for diluted ultrafine colloidal suspensions (Rulyov et al., 2005). Rulyov et al. (2005) carried ultra-flocculation studies on montmorillonite type clay suspensions and obtained very good results. They concluded that acceleration of the sedimentation rate increase twice, residual concentration of solids in water decreases by four to ten times, decrease the flocculant consumption by two to three times and the densification of the solid phase increases up to two times compared to the conventional flocculation process.

In conclusion, montmorillonite-rich tailings create significant waste management problems in minerals industry due to the colloidal character of montmorillonite mineral. To overcome this problem, flocculants should be supported with electrolytes, optimum pH and mechanical dewatering equipments in a proper flow-sheet.

2.6 Previous Studies on the Tailings of Kırka Boron Plant

2.6.1 Mineralogy of the Tailings of Kırka Boron Plant

The gangue minerals associated with boron minerals varying in type and amount show different separation behavior. Those water insoluble impurities are separated in the boron processing plant and boron is concentrated. Kırka tincal ore has minor amount of realgar, orpiment, gypsum, celestite, calcite, and high amount of dolomite and montmorillonite and relatively low amount of illite and chlorite is also associated with it (Inan et al., 1973).

Mineralogical composition of the tailings of Kırka Boron Plant is very important for many studies; the further beneficiation of the tailings, the alternative uses of the tailings which includes smectite clay, the dewatering and obtained strong and firm solid. To define mineralogical properties of the tailings, Kozulu (2003) and Kıpçak (2004) made X-Ray diffraction and chemical analysis on Kırka tailings. The XRD results of the tailings have showed “montmorillonite, dolomite, and borax” as main mineralogical constituents and the chemical analysis of the tailings have showed 27.69% SiO_2 , 4.58% Al_2O_3, 8.95% CaO, 12.45% MgO and 14.28% B_2O_3.

Kıpçak (2004) made a mineralogical analysis on the Kırka tailings and he found similar minerals with Kozulu (2003). The tailings mineralogical analysis indicated to smectite, dolomite, feldspar, calcite and very little amount of other carbonates and silicates.

Quantitative calculation of mineralogical analysis shows that the concentrator tailings contain 22-57% montmorillonite, 10-30% dolomite and max. 15% B_2O_3 (Garip, 2008).

The Research Department of the Eti Maden (Mergen et al., 2001) also verifies this result. It is said that montmorillonite is up to 55% and dolomite is up to 45% in the tailings. The mineralogy shows variations in type and amount and main gangue minerals montmorillonite and dolomite percentages may change but in conclusion, it can be said that the most abundant minerals in the Kırka tincal tailings are montmorillonite and dolomite.

2.6.2 Characterization of the Colloidal Phase of Kırka Tincal Solutions

Borates are generally not in pure state. Tincal minerals are generally found together with calcite, dolomite and clay minerals like montmorillonite and illite. Pure sodium borate can be obtained by removing the colloidal dispersed impurities from saturated hot tincal mineral solution. After tincal ore is removed from this solution by concentrating, suspended solid particles are subjected to flocculation for sufficient solid/liquid separation. Before detailed studies carried out, it was thought that the tincal solutions would have mostly clay type colloidal impurities in it. A study done by Akdeniz et al. (2003) proved that the actual situation was different. They did detailed SEM, XRD, FTIR test to identify this statement. After all these experiments , they concluded that colloidal phase did not include considerable amount of clay minerals but mainly dolomite in the colloidal phase and they stated that also this characterization will help to the effective and economic flocculation process with proper flocculant selection for dolomite.

2.6.3 Flocculation of the Clay Suspensions of Kırka Boron Plant

The dissolution stage of the Kırka Boron Plant produces borax solution. Impurities of tincal have no solubility and they are mostly clay and dolomite minerals in colloidal form. These colloidal impurities should be removed from the the plant waste stream. For this purpose, the insoluble slime is pumped to the thickener system. At the first thickener, 0.1% anionic Prestol 2620 (PAM) is used to thicken the slime. Then suspended particles are sent to the second thickener and here the pulp is treated with non-ionic AH – 912FH and FA308-F polyethylene oxide. At all stages, the cleaned water is recycled to the solution tank. Finally, the flocculated tailings material discharged to the tailings ponds.

Flocculation of the clay suspensions of Kırka Boron Plant is a major technical problem although three different flocculants are used in the present system. Disposal of the process effluents from the plant is gradually filling up the tailings ponds with insufficient solid/liquid ratio. The capacity of the tailings ponds can be increased by raising the height of the dikes surrounding ponds. Another solution can be to construct a new tailings dam. However these two options are temporary solutions of the problem (Çebi et al., 1994).

To find out a permanent solution, firstly mechanical dewatering like successive thickeners system and centrifugal decanters were studied but it showed that polymer addition was needed for the mechanical dewatering equipment even in the centrifuge decanter used to enhance solid-liquid separation (Çebi et al., 1994).

If Kırka tailings are not treated with polymers or mechanical dewatering techniques, it takes seven to ten days for sufficient sedimentation (Khan, 1980). This long period for sedimentation is not acceptable for a continuously working plant. For the Kırka tincal tailings, although some of the dewatering methods have been applied currently, they are not sufficient. Many different flocculation studies were carried out to improve this problematic tailings for the purpose of the proper disposal. The related parameters of these studies affecting the flocculation of Kırka tincal tailings will be explained in the following.

2.6.3.1 Polyacrylamide and Polyethylene Oxide Effect on Tincal Slime

The most common polymeric flocculants used in the processing plants are polyacrylamides and polyethylene oxides. As mentioned previously, the non-ionic polyethylene oxides and ionic polyacrylamides are more efficient than the cationic ones especially for clay tailings. In the Kırka Boron Plant, the anionic polyacrylamides are currently used at the first stage of thickening to flocculate relatively coarse tailings and similarly same type flocculants are applied in the USA BORAX Plant for the same purpose. Polyethylene oxide is generally used as second stage dewatering flocculants to flocculate fines and to decrease turbidity of waste water. It works in suspension with much lower solid ratio and effective for the clay particles to form dense strong flocs (Garrett, 1998).

PEO and PAM effect, and behavior on the tincal slime is very important for both dewatering purposes and recovery of the boron products. So, a comparative study between PAM and PEO was done by researchers. As explained previously, the plant tailings include mostly dolomite and montmorillonite. Flocculation behavior of these minerals is different from each other. It was claimed (Gür et al., 1996) that polyacrylamide was favorable in flocculation of montmorillonite-rich clay suspension whereas polyethylene oxide was favorable in flocculation of dolomite-rich clay suspension. In spite of this comparison, the great amount of polymer consumption was reported by Sabah and Yesilkaya (2000) (between 1 and 2 kg polymer consumption per ton). Although high amount of polymer was used (both polyacrylamide and polyethylene oxide), the turbidity values were still high and settling time was (Yüksel and Kurama, 2009) very long.

2.6.3.2 Coagulants Effects

The coagulants are used in thickening to help polymeric flocculants. For borax tailings, many coagulants were tested. In general, $Al_2(SO_4)_3$ and $FeCl_3$ are the most effective coagulants for dewatering (Pizzi et al., 2005, pp. 48-50). Those ones are studied to remove suspended solids in the wastewater of the Kırka clay suspensions because coagulation with lime, ferrous and aluminum salts has no important effect on boron but gangue minerals (Okay et al., 1985). The colloidal particles in the tailings are the major problem of flocculation process because the environmental regulation has a limit value in terms of the turbidity and the turbidity of the tailings in boron industry is above that limit with a value of 900 NTU (Yılmaz et al., 2006). In addition to the environmental consideration, the boron in the wastewater can be recovered if these insoluble colloidal particles are flocculated and removed from the solution. Yılmaz et al. (2006) tested $Al_2(SO_4)_3$ and $FeCl_3$ for Kırka tailings. Their performance was evaluated in terms of the turbidity. Whereas Alum decreases turbidity down to 2 NTU, $FeCl_3$ decreases the tincal tailings turbidity slightly higher values between 2-4 NTU. It is proved that $Al_2 (S\ O_4)_3$ is more effective than $FeCl_3$ and it is concluded with these coagulants the turbidity of borax tailings was removed by 99%. In conclusion, studies (Khan, 1980) showed that the order of the thickening efficiency of the electrolytes used for tincal slimes was $FeCl_3 < Al_2(SO_4)_3$. The combination of the coagulants was experimented and they were added at the same time into the suspension. This dual coagulant system resulted in poor turbidity removal (Köse and Öztürk, 2006). So, Al_2SO_4 was suggested for efficient solid / liquid separation (Yılmaz et al., 2006).

In the coagulation process of borax tailings, the most critical point is pH adjustment. In laboratory, coagulant experiments gave optimum results at pH = 5–6. Borax presence in the tailings can make pH adjustment (down to pH=5-6) difficult due to its buffering property. So, the flocculants were generally preferred to the coagulants in the wastewater treatment of the boron industry (Garrett, 1998) but the flocculation process can be enhanced with the help of a coagulant (Sabah and Yesilkaya, 2000).

2.6.3.3 Temperature Effect

The tincal is a very soluble salt in water. For beneficiation purposes, this property of the ore is used in the boron industry. In tincal plants, high temperature environment is used to make solid tincal ore soluble and separate from the insoluble clay and gangue minerals. Normally, the tailings temperature can be at high temperature in thickeners due to the hot solution processes. Gür et al. (1994) have made studies at 35^0 C and 65 ^{0}C. These studies showed that the increasing temperature caused increased reagent consumption up to three times of normal amount. Moreover, dolomite-rich sample becomes impossible to flocculate at high temperature (65 ^{0}C). This phenomenon revealed that temperature affects the physical adsorption of polymers on minerals.

2.6.3.4 Particle Size Effect

Kırka tincal tailings were analyzed in terms of the particle size. It was found that mostly clay size particle available in colloidal form. It was stated that the slime particles constitute important amounts of the tailings. The great percentages of -0,038 mm particles (% 96 of the tailings) leads to the high amount of polymeric flocculant consumption (Sabah & Yesilkaya, 2000) because very fine clay particles have a very large surface area. Moreoever, when particle size decreases down to clay size, the suspension shows colloidal form which is more stable and very difficult to flocculate.

2.6.3.5 pH effect

The salt deposits in Turkey have unique pH values. General pH trend can be summarized with the brines alkalinity from the northwest (gypsum matrix, pH < 7) to the southeast (borax, pH = 10), and then further east to Beypazari trona deposit (pH =10-11) (Garrett, 1998). The Kırka deposit is also located in the southeast and consistent with this tendency. When the working conditions of the Kırka Boron Plant are considered, it is seen that the actual pH value of the plant is around 9 (Sabah & Yesilkaya, 2000). This high pH leads to negatively charged dolomite and clay particles. Moreover, the boron adsorption on the species is maximized (Goldberg, 1997) at pH 9 and the already negatively charged surfaces become more negative. Around pH 9, the adverse effect of boron is promoted. In addition to this effect, the borates, especially sodium borates, are used as buffer in many processes, ranging from soil analysis (Pansu & Gautheyrou, 2006) to chemistry (Choo, 1994). In Kırka, a natural buffer solution at pH 9 is obtained (Sabah & Yesilkaya, 2000) when borax dissolved in the plant water stream. Due to the buffer feature of the solution, the pH adjustment was not studied and the original pH value was kept during the flocculation studies of Kırka tincal clays suspensions by several researchers (Khan, 1980; Sabah and Yesilkaya, 2000; Gür et al., 1994).

2.5.4.6 Boron Effect

Boron effects are common complicated discussion subject that was studied widely by researchers. Boron is specifically adsorbed on clay minerals and changes their physical properties. Some reports that the boron can be chemically bonded to the clay particles. Keren and O'Connor (1982) stated that boron can be specifically adsorbed on mineral surfaces through a mechanism referred to as ligand exchange, whereby the adsorbed species displaces H_2O from surface and forms partly covalent bonds with the structural cations. The boron adsorption mechanism was explained by (Keren et al., 1994) with two steps: The first step was a “rapid” adsorption of tetrahedral boron on the clay. The boron adsorption occurs mainly on the edge surfaces of the clay minerals. The second step is much slower diffusion in the tetrahedral sheet of the clay minerals. This step is called by the fixation. Those steps progress with aging. Whereas adsorption step lasts one day, the fixation lasts six months. Moreover, boron has an adsorption affinity for aluminum oxides and magnesium hydroxides. According to Goldberg (1997), availability of the calcium carbonate causes to increase in the boron adsorption and fixation on clay minerals and also $CaCO_3$ itself behaves as a boron adsorbing surface. This mechanism is very important in terms of the surface charge of clays and zeta potential because boron specific adsorption produces a shift in the isoelectric point (IEP) of the mineral (Goldberg, 1997). This means that at a certain pH the particles become more negatively charged after boron adsorption and fixation process.

Considering this boron-clay interaction, certain borax amounts were added to the flocculation experiments to identify its effect on the flocculation of Kırka tincal clays which mainly consists of clay minerals (Gür et al., 1994; Sabah and Yesilkaya, 2000). They confirmed the surface chemical properties changed in the presence of borax. Whereas Gür et al. (1994) reported that borax concentration increase leads to decrease in turbidities of supernatants and polymer consumptions, Sabah and Yesilkaya (2000) reported just the opposite. Sabah and Yesilkaya (2000) stated that increasing borax concentration lead to increase in adsorption and absolute value of the negative zeta potential on the particles also increased. As a result of this, it was more difficult for anionic polymer attachment on the negatively charged particle surface and the effectiveness of flocculation weakened.

Noirot (1998) also confirmed adverse effect of borax and stated that “the effects of soluble borates on colloidal systems are distinct from simple organic salts and in some circumstances borates appear to behave as mild deflocculants*”*. Sabah and Yesilkaya (2000) agreed with Noirot (1998) and the reason of the difficulties in the flocculation of Kırka clay suspensions was explained with this deflocculation property of borax. They claimed that the high flocculant consumption in the Kırka Boron Plant, which varies between 1000 – 1500 g per ton solid waste, stemmed from this adverse effect of borax presence in the tailings.

CHAPTER 3

MATERIAL AND METHODS

3.1 Material

Two kinds of samples containing clay were collected from the Kırka tincal mine for carrying out separate laboratory flocculation tests with the major components of this problematic waste stream of the tincal processing plant. One of the samples was taken from montmorillonite-rich clay layers of the mine and referred to as the green clay sample; and the other one was taken from dolomite-rich clay layers and referred to as the white clay sample, in accord with their native color.

Certain amounts of the clay samples were treated with 1M HCl acid to differentiate soluble species (carbonates) and insoluble species (silicates). Following the acid treatment, the samples were dried and weighed again. Undissolved part of the green clay sample was % 68 of the initial sample amount whereas undissolved part of the white clay sample was % 22 of the initial sample amount after HCl treatment. The results of the acid treatments verified that the green clay was rich in montmorillonite and the white clay rich in dolomite (other non-clay minerals were not taken into consideration due to their small amounts). Characteristics of these two samples are presented in the following sections.

3.1.1 Particle Size and Surface Area of the Samples

As-received samples were dispersed in water by stirring in an attrition scrubber for 3 minutes and then screened through a 37 μm sieve. The particle size analyses of the green sample, white sample and the actual tailings of the plant (which was previously determined by ETİ Maden) was plotted as shown in Figure 10.

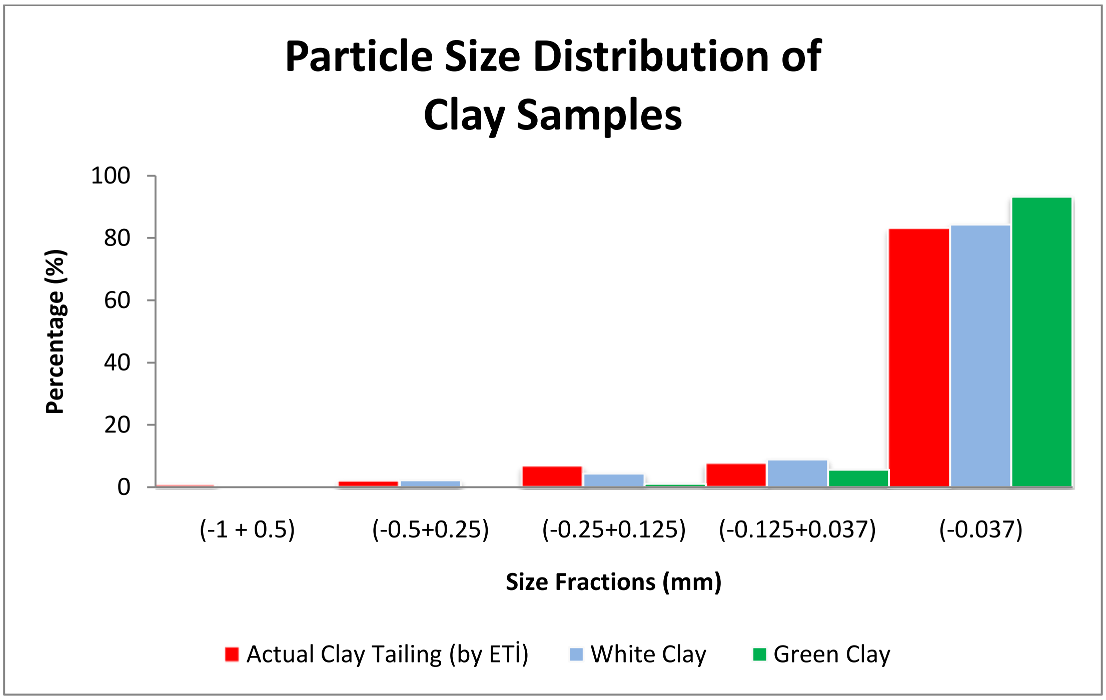


Figure 10. Particle Size Analysis

BET analyses were carried out with Quantachrome Corporotion – Autosorb 6 surface characterization equipment. The samples were prepared to eliminate surface water and moisture by applying heat treatment. Then, the samples were weighed (0.23 g) and placed on the holders. The powders were measured at a pressure of $P / P_0 = 0.31$ by using nitrogen as analysis gas for the purpose of determination of the surface areas.

The measurements (Table 1) showed that the surface area of the green clay sample was almost two times greater than the white clay. The superiority of the green clay over the white clay was very normal because of the grain size, the variation in the amount of clay and non-clay minerals.

Table 1. BET Analyses of the Clay Samples

Sample	**Surface Area**
Green Clay	19.77 m^2 / g
White Clay	10.90 m^2 / g

3.1.2 Chemical Analysis of the Clay Samples

The chemical analyses of the samples were determined with benchtop X-Ray Fluorescence Spectrometer. The results were given in Table 2.

Table 2. Chemical Analysis of the Clay Samples

Constituent	**Green Clay (wt %)**	**White Clay (wt %)**
SiO_2 - Silicon Oxide	26.94	15.35
Al_2O_3 - Aluminum Oxide	5.00	0.43
Fe_2O_3 - Iron Oxide	1.90	0.21
MgO - Magnesium Oxide	15.28	22.00
CaO - Calcium Oxide	16.36	28.47
Na_2O - Sodium Oxide	1.52	1.91
K_2O - Potassium Oxide	3.72	0.29
SrO - Strontium Oxide	1.53	2.26
LOI - Loss on Ignition	20.08	38.75

According to the chemical analyses, the green clay sample has higher SiO_2 percentage (26.94%) than the white clay sample (15.35%). On the other hand, the white clay sample has higher CaO (28.47%) and MgO (22.00%) than the green clay sample CaO (16.36 %) and MgO (15.28 %). In addition to that, small amount of potassium, strontium, sodium, iron and aluminum were available in the samples.

3.1.3 Mineralogy of the Green Sample

X-Ray Diffraction Pattern (random sample) of the green clay was loaded to MAUD (Material Analysis Using Diffraction) Refinement Program for the purpose of mineralogical analysis. Then, the actual pattern was compared to the standard pattern of the minerals. It was observed that some differences exist in intensity, peak position, peak width, background, scale and 2θ degrees. To refine pattern and eliminate differences, the MAUD Wizard was run. The standard peak positions of expected minerals and the calculated ones were tried to be synchronized. This process was carried out successfully and this was proven visually by 2-D Multiplot in Figure 11.

After MAUD Refinement, X-ray pattern was plotted as shown in Figure 12. The identified peaks refer to mainly smectite type clay mineral (possibly, montmorillonite) and dolomite. The less intense peaks indicate the small amount of K-feldspar and illite minerals. All of these minerals were labeled according to different colors and their refined peaks were drawn by the program (Figure 12) according to the defined colors.

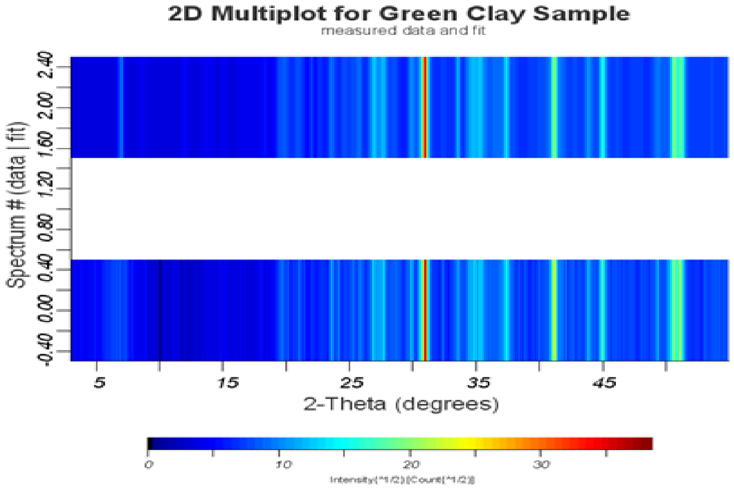


Figure 11. Eliminated Residual Differences of the Green Clay Sample with MAUD

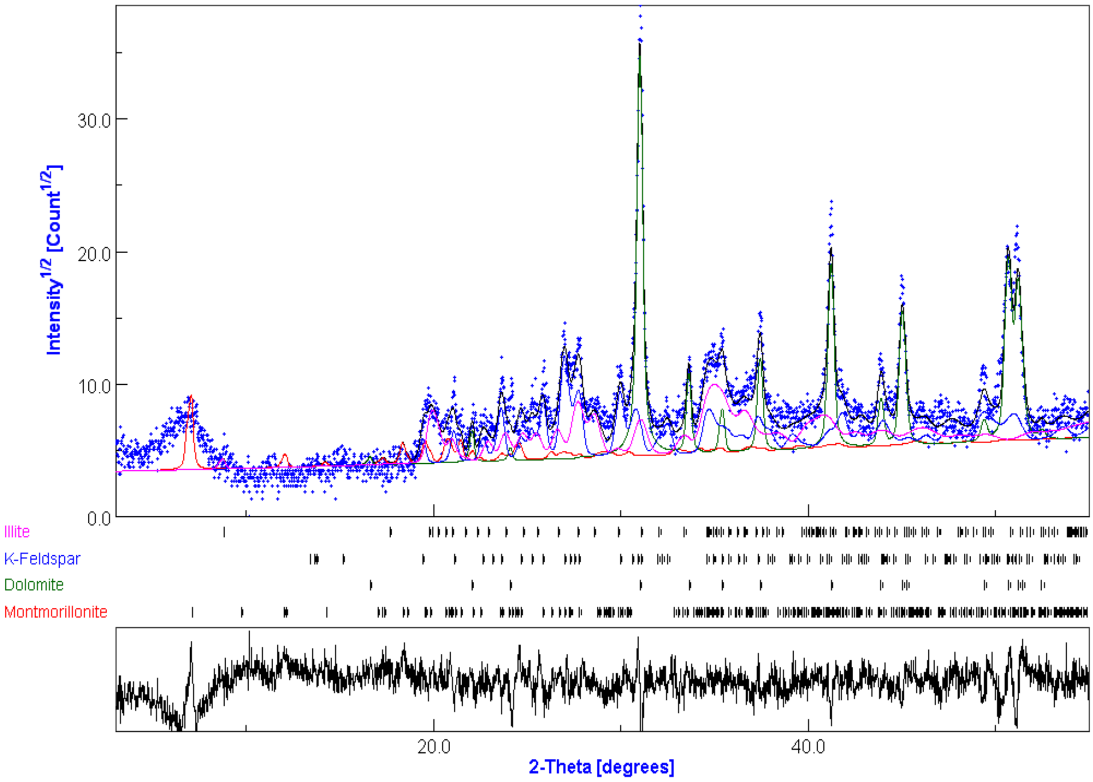


Figure 12. MAUD Results of the Green Clay (Random Sample)

MAUD refinement result of the green clay also gave information about crystal structures of minerals (Table 4 and Table 5).

Table 3. Montmorillonite Crystal Structure in the Green Clay Sample

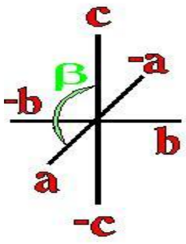
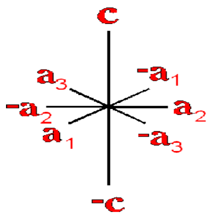
Montmorillonite in Green Clay	**Crystal System: Monoclinic**		**Standard Cell Dimensions (Å)**	
	Cell Dimensions ± Error (Å)			
a	5.1978	0.0296	5.1700	
b	9.0611	0.0679	8.9400	
c	12.400	0.0250	10.0000-15.0000	
d(001)	12.400		10.0000-15.0000	

Table 4. Dolomite Crystal Structure in the Green Clay Sample

Dolomite in Green Clay	**Crystal System: Trigonal**		**Standard Cell Dimensions (Å)**	
	Cell Dimensions ± Error (Å)			
a	4.8012	0.0015	4.8420	
c	15.9700	0.0047	15.9500	
d(104)	2.8820		2.8860	

The peaks of dolomite and K-feldspar are very sharp and these minerals easily identified according to XRD pattern. However, a very broad peak is obtained at 12.40 Å and the reason of this is the carbonate coating on the clay minerals. This broad peak most probably belongs to smectite group clays but, a detailed mineralogical analysis carried out for the green clay sample in the following section to prove and identify montmorillonite presence.

Smectite group minerals give their differential peak at d(001) and this corresponds also to c-axis of its cell dimensions. For identification purpose, the dimension of c-axis is very important due to its swelling property. In general, its range lies between 10 and 15 Å. This change stems from the hydration degree, humidity, water molecules in interlayer space, size and charge of the interlayer cations. (Çelik and Karakaya, 1998). d(001) is calculated as 12.40 Å in X-ray diffraction experiments. As a result, it may be claim that smectite type clay mineral has a hydrated interlayer in the untreated powder form (Chen, 1977; Çelik and Karakaya, 1998).

The crystal structure (Table 5) of the dolomite in the green clay sample proved that it is an ideal dolomite. In general, carbonate minerals (mainly, calcite) take magnesium in its crystal structure from environment and subjected to contraction because Mg-ion is smaller than Ca-ion and this process called dolomitization (Tucker and Wright, 1990). Its c-axis dimension is contracted from 17 Å to 16 Å and a-axis dimension from 4.99 Å to 4.80 Å (that is 15.97 ≈ 16 Å for c-axis and exactly 4.80 Å for a-axis dimension in dolomite mineral of the green clay) during dolomitization. The differential peak d(104) also indicates to 2.88 Å (Özpeker and Çoban, 1991;Akkoca and Kalender, 2007), which define dolomite mineral as "ideal dolomite" and it can be concluded that equal amount of Ca and Mg present in the crystal structure of the dolomite.

3.1.3.1 Identification of the Actual Clay Material in the Green Sample

To identify clay minerals, ethylene glycolation and heat treatment were applied to the green clay samples because the XRD results of the random sample gives sufficient information about non-clay minerals but not for clay minerals. The green sample was prepared prior to the ethylene glycolation and heat treatment. Firstly, the clay sample was mixed with water in a beaker. In this beaker, the acid treatment was done in very dilute acid concentration (0.1 M HCl) to eliminate carbonate minerals (dolomite) that coats clay minerals because the presence of carbonate coatings make interpretation of diffraction patterns difficult. This acid treatment procedure was maintained for one week by mixing in a magnetic stirrer. Then, the suspensions were left to settle down for 8 – hours. The unsettled part was taken into another beaker. After this suspension was centrifuged, 2 – 3 drops of the centrifuged suspension placed on the four different glass slide so that the liquid covered the entire surfaces of the each slide. The slides, which have four identical samples on them, were put on a leveled surface and kept still until completely dried at room temperature. During this procedure (drying) clay platelets were sedimented and oriented on top of each other basal surfaces. First slide labeled as AD (air-dried) and it was untreated, the second slide labeled as EG for ethylene glycolation, third and forth slides labeled 300 °C and 500 °C for the heat treatment. The samples on the glass slides were used for the identification of the actual clay materials in the green sample.

The (untreated) air-dried oriented sample was placed on the holder of XRD equipment and analyzed before the treatments. The possible smectite peak of AD-X-ray pattern (Figure 13) seems to be depressed strangely. It may indicate that the carbonate minerals still exist and making the interpretation of the peaks by coating the clay minerals difficult. However, 10 Å peak indicates to illite mineral. Furthermore, the other non-clay mineral like feldspar still exist in the clay fraction that means feldspar particle sizes were also very fine.

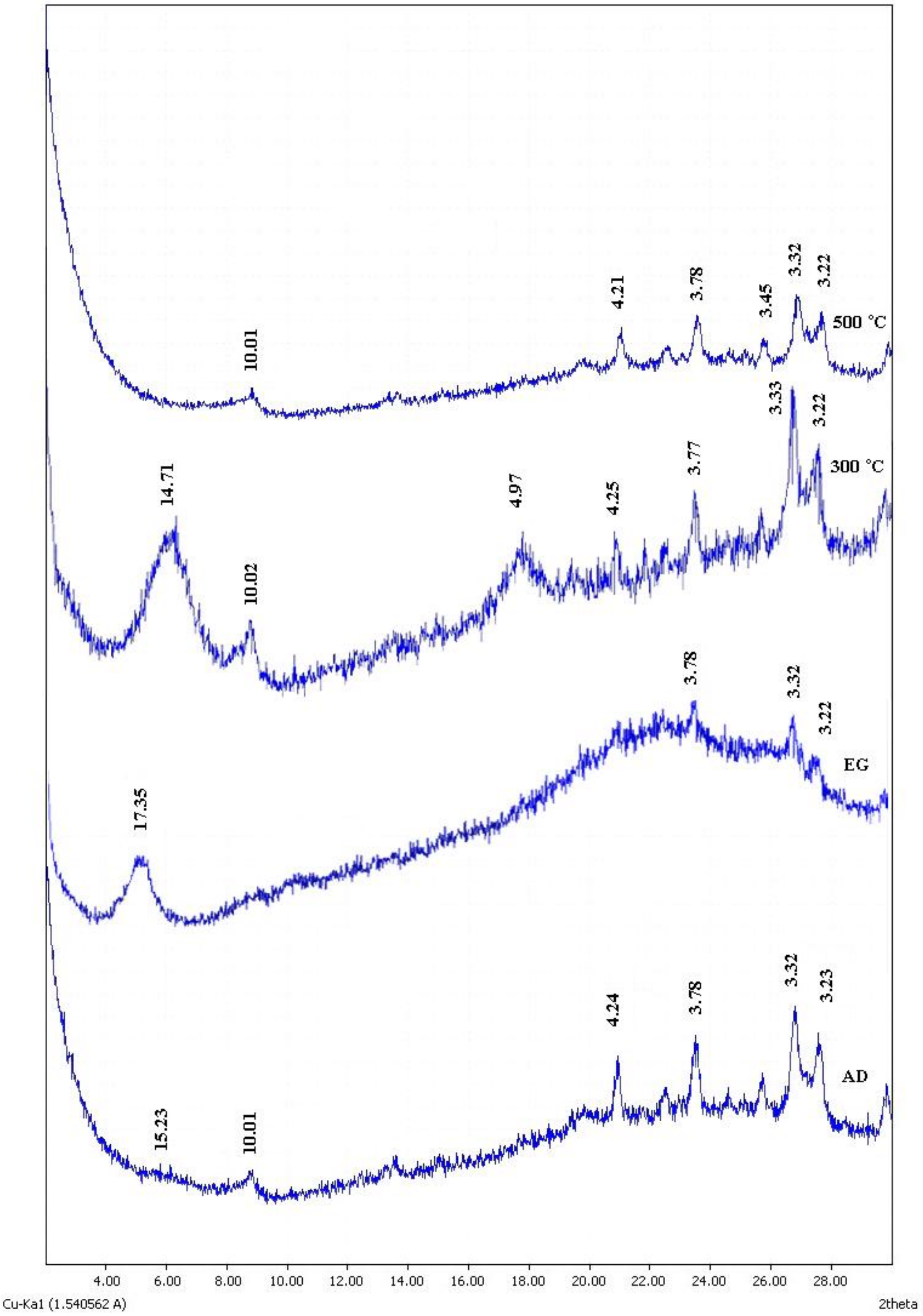


Figure 13. X-Ray Diffraction Patterns of the (Oriented) Green Sample (AD: Air-Dried, EG: Ethylene Glycol, Heating to 300 °C and 550 °C)

The most specific property of the smectite type clay is the swelling. In clay mineralogy, this swelling property is used to identify the clay minerals. EG-labeled glass slide of the green sample was subjected to the ethylene glycol vapor at 60 °C for 6 hours and the diffraction pattern was analyzed. Figure 13 proved the presence of montmorillonite after the ethylene glycolation (EG) procedure. d(001) diffraction of the montmorillonite increased from 12.40 Å (random sample) to 17.35 Å (EG) (Figure 13) after EG-treatment because ethylene glycol molecules enters into the interlayer spaces of montmorillonite and this resulted in the increase of (001) direction of the clay mineral (swelling).

For the further analysis, the green sample was subjected to the heat treatment at 300 °C. It was expected at this temperature that the montmorillonite mineral collapsed down to 10 Å. But, the mineral showed resistance to the heat and collapsed from 17.35 Å down to 14.71 Å (Figure 13) instead of 10 Å by heating at 300 °C. This may be explained with the release of cations, especially Mg due to the small radius, from the dolomite mineral (after the acid treatment) that enters the interlayer space of the montmorillonite and it may resist to collapsing by forming an aqua-complexes inside (like a pillar). 10.02 Å peak was also observed at this temperature and it may refer to the small amount of illite type clay minerals.

Further heat treatment was carried out for the green sample at 500 °C. When the diffraction patterns of the ethylene glycolation and the heat treatment at 500°C (Figure 13) were compared, the montmorillonite was collapsed completely down to 10 Å and its structure of it resembled illite mineral. Moreover, the background was seriously decreased and feldspar peaks were clearly observed (Figure 13).

3.1.4 Mineralogy of the White Sample

X-Ray Diffraction Pattern of the white clay (random sample) was loaded to MAUD Refinement Program for the purpose of mineralogical analysis. The analysis of the white clay sample was carried out similar to the green clay. The same procedure (Figure 14) was applied to the white clay sample and the results were explained in the following.

X-ray pattern of the white clay was refined by MAUD program as shown in Figure 15. The diffraction pattern showed that mainly dolomite (and possible smectite type clay minerals). The less intense peaks may indicate small amount of illite mineral. All of these minerals were labeled in Figure 15.

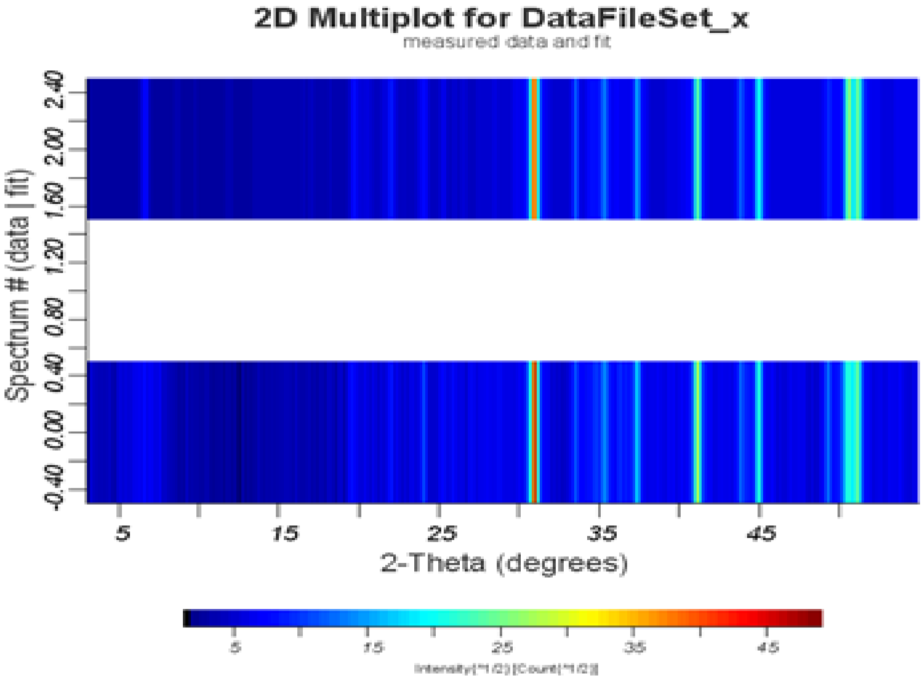


Figure 14. Eliminated Residual Differences of the White Clay

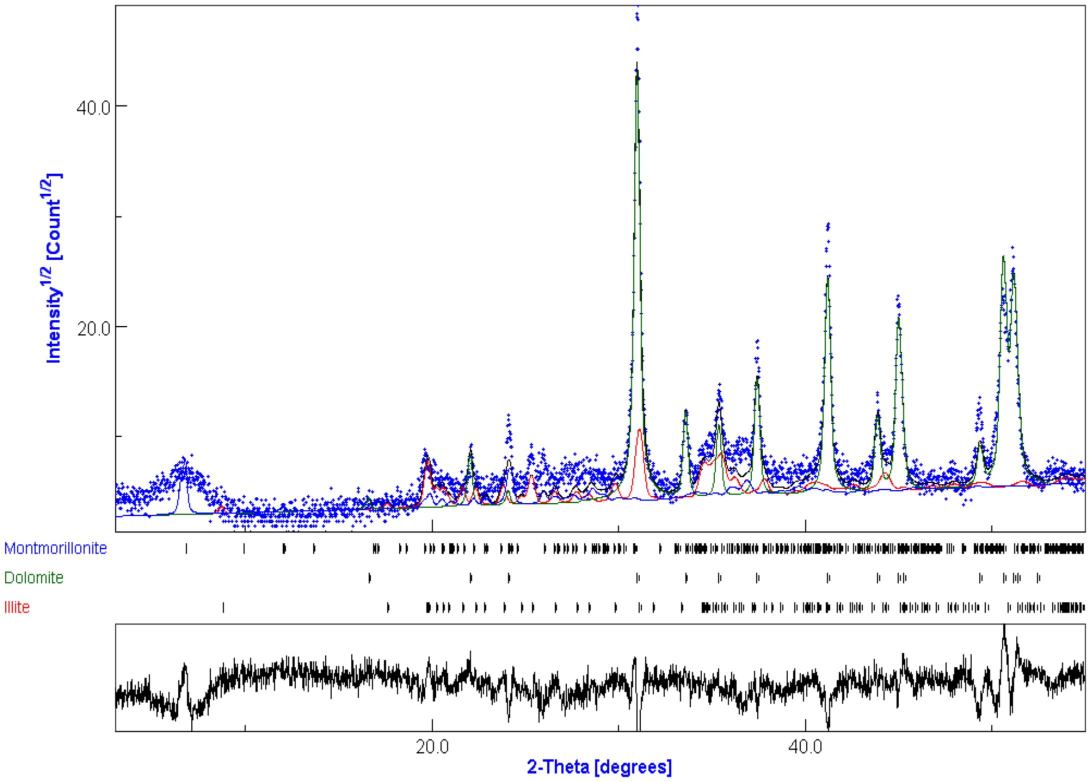


Figure 15. MAUD Results of the White Clay (Random Sample)

MAUD refinement results of the white clay samples also gives information about crystal structures of minerals (Table 5 and Table 6).

Table 5. Montmorillonite Crystal Structure in White Clay

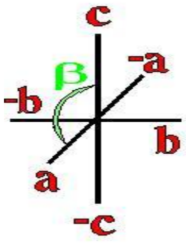
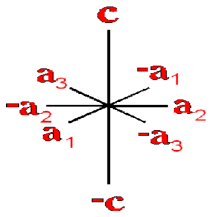
Montmorillonite in White Clay	**Crystal System: Monoclinic**		**Standard Cell Dimensions (Å)**	
	Cell Dimensions ± Error (Å)			
a	5.1802	0.0286	5.1700	
b	8.9187	0.0628	8.9400	
c	12.9548	0.0297	10.0000-15.0000	
d(001)	12.9548		10.0000-15.0000	

Table 6. Dolomite Crystal Structure in White Clay Sample

Dolomite in White Clay	**Crystal System: Trigonal**		**Standard Cell Dimensions (Å)**	
	Cell Dimensions ± Error (Å)			
a	4.8032	0.0005	4.8420	
c	15.9955	0.0002	15.9500	
d(104)	2.8841		2.8860	

From Figure 12 and Figure 15, it can be seen that the mineralogy of the white clay minerals is similar to the green clay with small differences. The background is depressed to lower intensity values. So, the data calculation and interpretation is relatively easy and this gives more accurate results in mineral cell dimensions, especially in dolomite. Moreover, the montmorillonite differential peaks depressed and dolomite peaks become sharper and more intense. Regarding these results, it may be concluded that dolomite becomes more dominant mineral in white clay, relatively.

Smectite type clays give its differential peak at d(001) and 12.95 Å peak may refer to smectite in X-ray diffraction experiments. As it mentioned previously, d(001) corresponds to the c-axis of the mineral and this dimension define the swelling property. According to some researchers (Çelik & Karakaya, 1998) and (Chen, 1977), this d(001) value may indicate to presence of water molecule or cations in the interlayer space.

Dolomite crystallinity degree increases in white clay according to the green clay. It can be observed on the X-ray diffraction pattern; the intensity of the dolomite increases and the error margin decreases to lower values. When the cell dimensions are compared to a calcite mineral, it can be seen that expected contraction is eventuated completely. Considering d(104) = 2.88 Å, it can be said that the dolomite is an “ideal dolomite” in terms of crystal structure.

3.1.4.1 Identification of the Actual Clay Material in the White Sample

The white clay samples were prepared in the same way of the green sample prior to the detailed XRD analyses for the purpose of the identification of clay mineral. The suspended particles decanted into a beaker and acid treatment was applied (0.1 M HCl) to dissolve dolomite coatings. After 8 – hours sedimentation, the unsettled part was separated (clay fraction) and the suspension was centrifuged. Then, the water – clay mixture was pasted on the four glass slides and dried in room temperature to obtain oriented samples. These four glass slides were labeled as

AD, EG, 300°C and 550°C and the required treatments were applied to these slides according to their labels.

The (untreated) air-dried labeled slide was placed on the holder of XRD equipment and analyzed before the treatments. The smectite peak was easily stated at 2theta = 5.54 (Figure 16). It can be said that it took water molecules or cations inside the interlayer and swelled to 15.95 Å during the sample preparation. However, this is not sufficient to name the swelling type mineral.

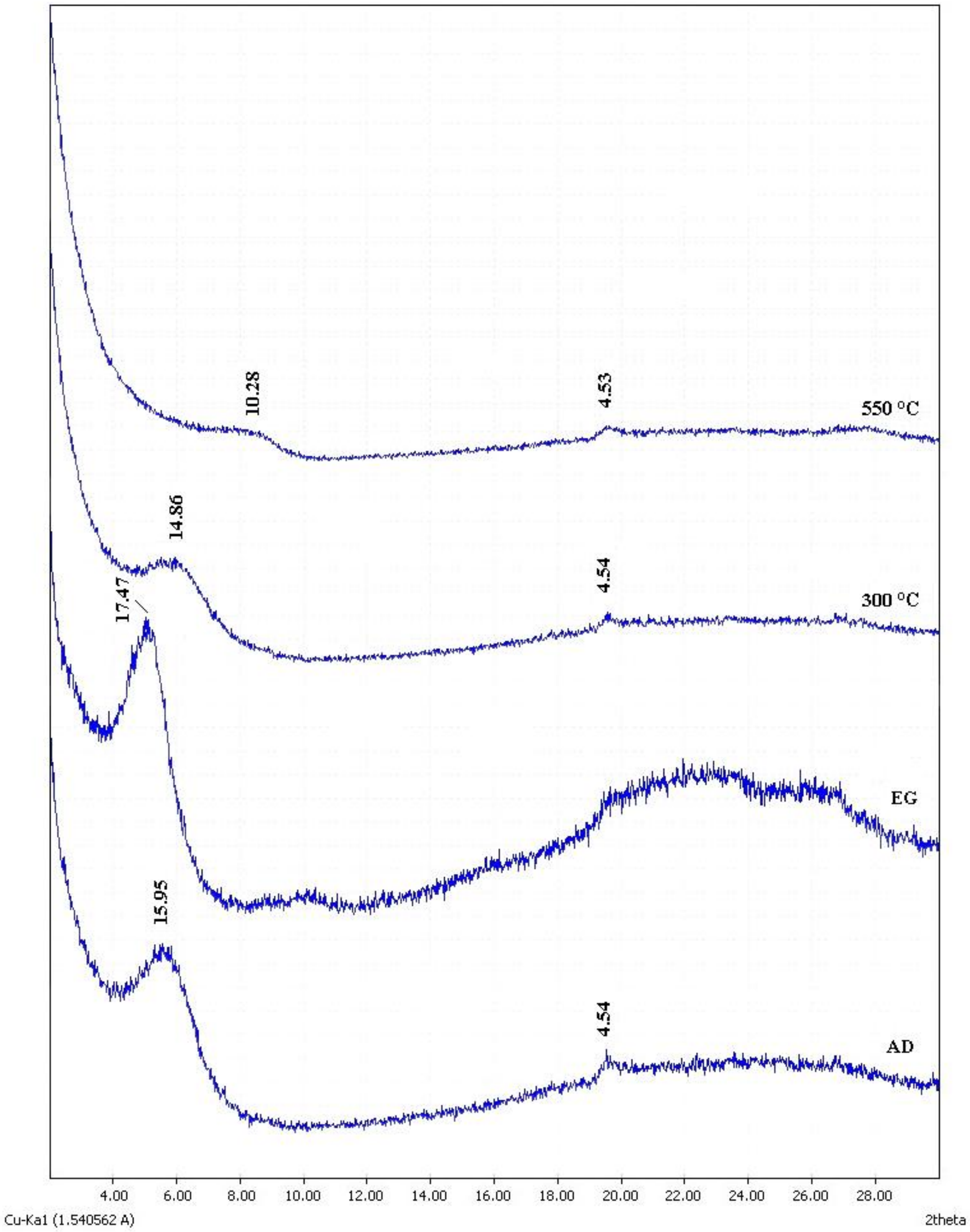


Figure 16. X-Ray Diffraction Patterns of the (Oriented) White Sample (AD: Air-Dried, EG: Ethylene Glycol, Heating to 300 °C and 550 °C)

Moore and Reynolds (1997) stated that smectite type clay minerals are identified with Ethylene Glycolation (EG) because EG treated swelling type clay minerals give very strong 001 reflection around 2theta = 5.2. Ethylene glycolation treatment was applied to the white clay sample at 60°C. After the procedure was completed, the XRD result was analyzed as shown in Figure 16. According to the EG-pattern, the intensity of the (001) peak at 2theta 5.2 and the height of clay mineral increased and shifted slightly to the left. This indicated to the presence of montmorillonite because of the swelling from 12.90 Å (random sample) to 17.47 Å (ethylene glycol treated oriented sample) as shown in Figure 16.

At 300 °C, the heat treatment was carried out. The peak was expected to collapse to 10 Å but as stated below montmorillonite in the white clay did not. It decreased down to 14.86 Å at 2theta 5.94 (Figure 16). This may stemmed from the cations entering the interlayer space which resists collapsing effect of heat treatment. Moreover, the background was also depressed.

At 550 °C, further heat treatment analysis was carried out. The background was decreased and only two peaks were detected. The peak location was shifted to the right at 8.60° - 2theta and d value decreased to 10.28 Å due to collapse of the montmorillonite as shown in Figure 16.

3.1.5 Mineralogical Compatibility of the Clay Samples

X-Ray Fluorescence, X-Ray Diffraction methods were applied to the clay samples and mineralogical analysis were carried out by using MAUD Refinement Program. As a result of mineralogical analysis, the characteristics of the minerals were studied.

Regarding smectite group main mineral montmorillonite, it was proved that the interlayer space of clay mineral did not collapse and the swelling property of the montmorillonite mineral was still kept considering the crystal structure in both green and white clay. Collapse of clay mineral is very important because once the interlayer space collapsed the swelling property may be lost permanently or swelling behavior change and this statement may become irreversible (Ertem, 1971; Olphen, 1967). The collapsing of the montmorillonite may completely change the flocculation behavior of the suspensions including montmorillonite. For this reason, the preservation of the swelling character of the montmorillonite is very important in terms of the flocculation studies.

Regarding dolomite mineral, it was proved that the dolomite completed its dolomitization process and reach to the “ideal dolomite” crystal structure. It is known that similar clay depositions in Turkey (Yalçın and Karslı, 1998; Özpeker and Çoban, 1991) show sometimes Ca – Dolomite (known also proto-dolomite) characteristics. The selection of clay minerals including ideal dolomite (Ca amount is equal to Mg in the ideal dolomite) is very important in terms of the flocculation studies because the variation of Ca and Mg amounts in the crystal structure changes the solubility, surface behavior, hydration degree and surface species of the dolomite.

In conclusion, the green clay and the white clay collected from the tincal mine are very suitable to carry out laboratory flocculation tests that reflect montmorillonite-rich and dolomite-rich wastestream of the Kırka Boron plant (Garip, 2008; Garrett, 1998; Gür et al., 1994; Khan, 1980) in terms of the mineralogical constituent.

3.1.6 Flocculants Used in the Experiments

The flocculants used in the experiments and their properties are shown in Table 7. UMA Magnafloc (polyacrylamide) was provided by Ciba Specialty Chemical, polyethylene oxide was provided by the Management of Kırka Boron Plant (SNF Floerger) and Enfloc (polyacrylamide) provided by ECS Kimya.

Table 7. Flocculants Used in the Experiments and their General Properties

Flocculant Name	**Flocculant Type ***	**Molecular Weight ***	**Physical Form**	**Particle Size**
MagnaFloc 4240 (Polyacrylamide)	Anionic	High Molecular Weight with UMA Technology	Powder	98% < 1000µ
Polyethylene Oxide	Non-Ionic	High Molecular Weight	Powder	100% < 1000µ
Enfloc230N (Polyacrylamide)	Non-Ionic	High Molecular Weight	Powder	95% < 1000µ
Enfloc320A (Polyacrylamide)	Anionic	High Molecular Weight	Powder	95% < 1000µ

* **Proprietary data unrevealed by the manufacturers.**

3.1.7 Properties of the Tap Water and the Distilled Water used in the Flocculation Experiments

The tap water of METU was periodically analyzed by the Department of Environmental Engineering. The chemical constituents of the tap water were given in Table 8. The amount of Ca ions in the tap water is very high with 151 mg / L. The amount of magnesium ions in the tap water is remarkable with 26.3 mg / L.

Table 8. Analysis of Tap Water in METU Campus

Parameters	Unit	Tap Water in METU Campus*
Cr	mg / L	< 0.02
Pb	mg / L	< 0.001
As	µg / L	< 1.0
Se	µg / L	< 1.0
Cd	mg / L	< 0.001
F	mg / L	0.34
Cl	mg / L	54.5
SO_4	mg / L	147
Fe	mg / L	0.042
Mn	mg / L	< 0.03
Cu	mg / L	< 0.001
Zn	mg / L	0.011
Ag	mg / L	< 0.005
Ca	mg / L	151
Mg	mg / L	26.3

*** Periodic Tap Water Analysis (Report Date: 05.07.2010) of METU Campus done by the Department of Environmental Engineering**

The general properties of the tap water were also determined with Lovibond SensoDirect Con200 Conductivity/TDS/Salinity Meter and stated in Table 9. The most important difference is the amount of total dissolved solids (TDS) in the tap water with 552 mg / L that leads to the great hardness of tap water. In addition to that, high TDS value of the tap water seems to decrease the specific resistance and increase the conductivity.

Table 9. General Properties of the Tap Water and the Distilled Water

Water Properties	Salinity	Total Dissolved Solid	Hardness	Specific Resistance	Conductivity	pH
Distilled Water	0.0 g / kg	3 mg / L	Very Soft (1 °F)	-	3.6 µS	7.00
Tap Water	0.3 g / kg	552 mg / L	Very Hard (36.4 °F)	1845 kOhm	565 µS	7.23

3.1.8 pH of the Clay Suspensions

pH measurements were carried out right after the simulated pulp was prepared upon addition of the clay samples in borax solutions. The experiments showed that borax availability in the clayey pulp instantly increased and fixed pH to around 9.40. The actual tailings has pH of around 9.0 – 9.4 (Khan, 1980). This phenomenon is valid for all borax solutions and it was explained by previous researchers (Somasundaran & Moudgil, 1987) that the borax buffers the solutions, maintaining pH around 9.3. In conclusion, additional pH adjustment was not required for clay suspensions due to the addition of borax.

3.1.9 Zeta Potential of the Clay Samples

The zeta potential of the green clay and white clay particles were measured with Zetasizer Nano-Z meter in the Mineral Processing Laboratory of Mining Engineering Department of METU. For the measurements, 0.3 g sample was weighed and put into 100 ml distilled water and the suspension mixed continuously and dispersed with a magnetic stirrer. pH of the clay suspensions were adjusted to required values with the addition of 0.1 M HCl and 0.1 M NaOH solutions. After pH adjustment, the suspensions were injected into disposable cuvettes of the instrument (Figure 17).

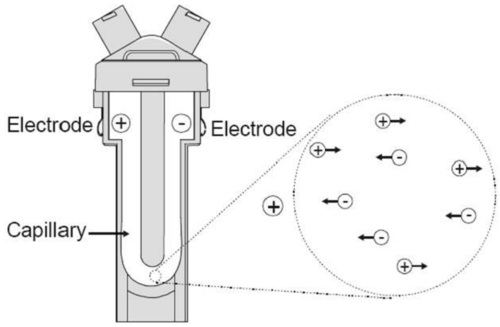


Figure 17. Disposable Cuvette of Zetasizer Nano-Z Meter and Particle Movement According to Electrode Sign

Then, the disposable cuvettes were placed in Zetasizer and zeta potentials of clay samples at different pH values were measured at room temperature (24 – 25 °C). The results were plotted in Figure 18.

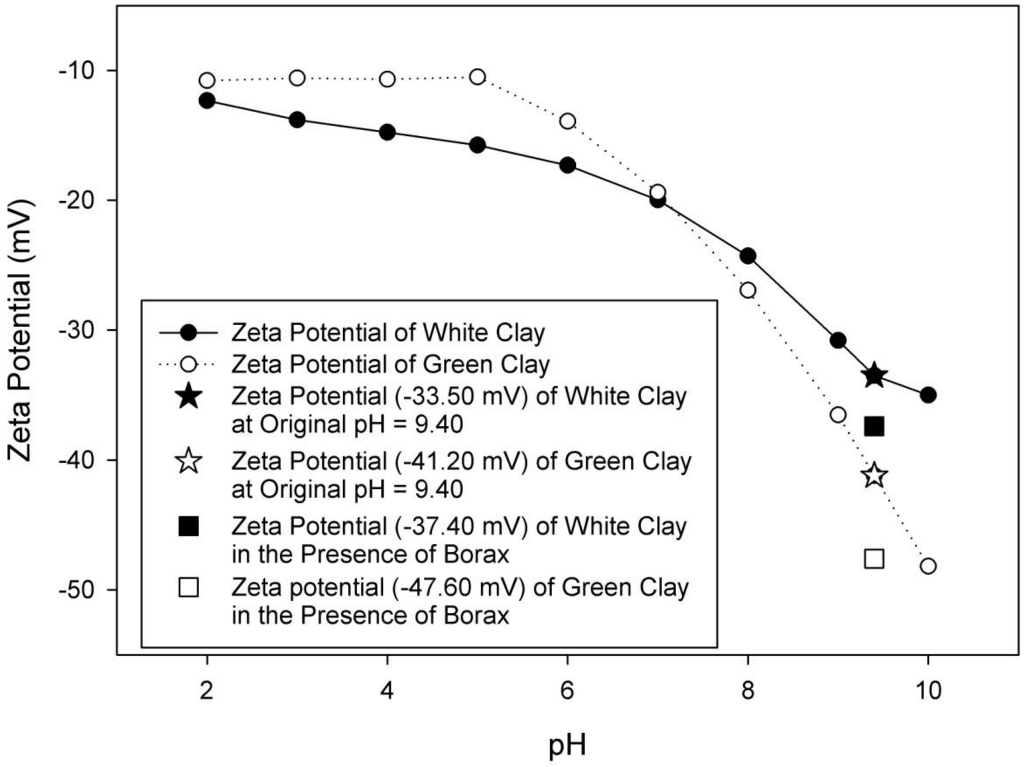


Figure 18. Zeta Potential Measurements of the Clay Samples: 0.3 g clay dispersed in 100 ml distilled water (only for borax effect, in 100 ml of 0.3% borax solution)

IEP values of the clay samples could not be found because zeta potentials had always negative values within pH range of the experiments. Similarly, IEP of pure montmorillonite samples (Benna, 1999) (or montmorillonite samples with high carbonate content (Hançer, 1994)) could not be found by some researchers. So, they preferred to express isoelectric point $pH_0 < 2\text{-}3$ (Taubaso et al., 2004; Sondi et al., 1996; Kosmulski M. , 2009). Depending on these researchers' expressions, it can be said that pH_0 values were lower than 2 (if any) for both green and white clay types because all zeta potential measurements were found negative throughout the studied pH range.

Also, it can be seen that zeta potentials of both clays were relatively stable around -10 mV and -15 mV between pH 2 and pH 7 but increased significantly from neutral to higher pH 10. The original tailings pH was considered and zeta measurements were carried out at pH = 9.40 for both clays. Zeta potential of green clay was found as -41.20 mV and zeta potential of white clay was found as -33.50 mV at original pH of the tailings.

The zeta potential measurements were also carried out in the presence of borax (pH = 9.40). For the measurements, 0.3 g sample was weighed and put into 100 ml distilled water including 0.3 g dissolved borax and the suspension mixed continuously and dispersed with a magnetic stirrer. The zeta potential of the green clay decreased from -41.20 to -47.60 mV and the zeta potential of the white clay decreased from -33.50 to -37.40 mV due to borax addition (Figure 18). It was clearly observed that borax presence makes the surfaces of both clay samples more negatively charged.

In conclusion, it can be said that the montmorillonite-rich green clay had more negative surface charge than the dolomite-rich white clay, exclusively at pH 9.40.

3.2 Methods

3.2.1 Flocculation Tests

Preliminary flocculation experiments were tried with hand shaking of graduated cylinder. However, the polymer and the clay suspensions could not be mixed successfully. The turbidity could not be removed. In addition to that the flocs had a very loose structure as shown in Figure 19. The picture was taken after 30 minutes sedimentation time and this photo reveals fiber like weak - thin structure of the flocs (Figure 19). Therefore, the flocculation tests were carried out under mild agitation and flocs became more dense and strong by increasing the probability of polymer – particle collision (Bulatovic, 2007).

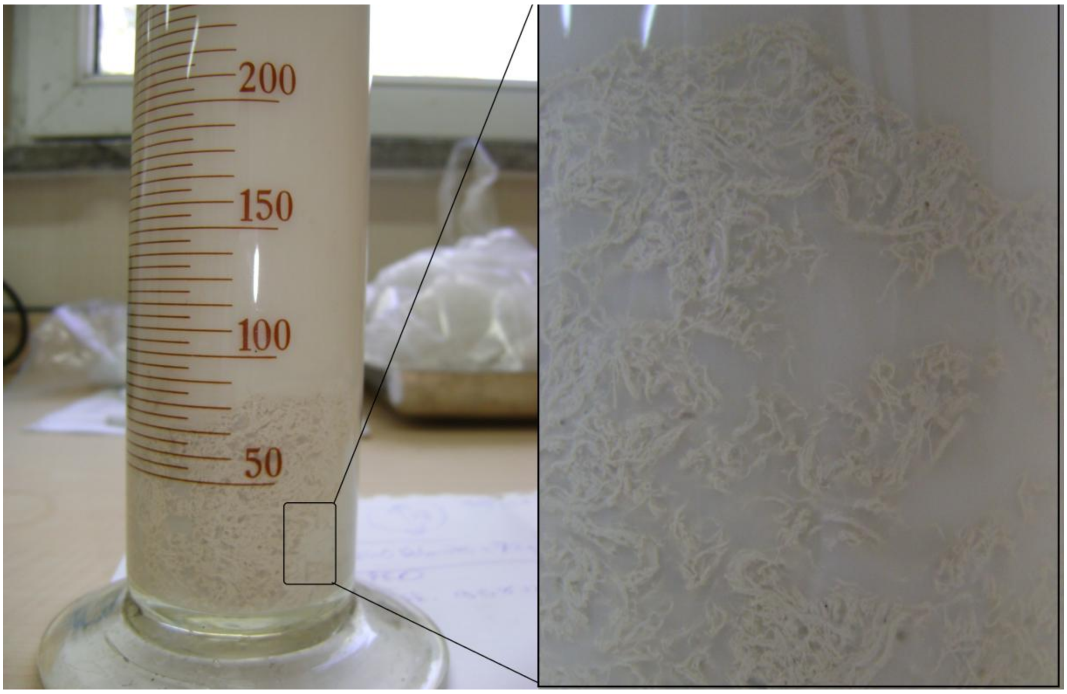


Figure 19. Hand Mixing of Polymer and Pulp (Picture was taken at the end of the 30 minute-period; 100 ml-UMA Magnafloc; 3% Clay; 3% Borax; pH=9.40)

Flocculation tests were conducted with suspensions containing 3%, 10 % and 15% by the weight of the clay sample solids in 300 ml of 3%, 10 % and 15% borax solutions. The suspension was intensely stirred at 1000 rpm for 3 minutes in an attrition scrubber to thoroughly disperse the clay sample. Then, the suspension was transferred into a 800 ml graduated beaker and stirred mildly at 150 rpm. 0.01% solutions of the UMA Magnafloc flocculant (or other conventional polyacrylamide and polyethylene oxide flocculants) were added to obtain required dosages and the suspension was further stirred for floc formation for 3 minutes. Then, the flocculated suspension was poured into 500 ml graduated cylinder (Figure 20) and was allowed to settle for 20 minutes. At the end of the 20 minutes period, the turbidity measurements were carried out. The turbid water sample of 10 ml volume was withdrawn from a fixed depth in the turbid supernatant with the help of a glass pipette. Then, this turbid water was transferred into a measurement glass and the glass was placed in the holder of a Lamotte Model Portable Turbidimeter. The measurements were expressed in nephelometric turbidity units (NTU). This UMA Magnafloc or conventional flocculants treatment was called as the first stage flocculation.

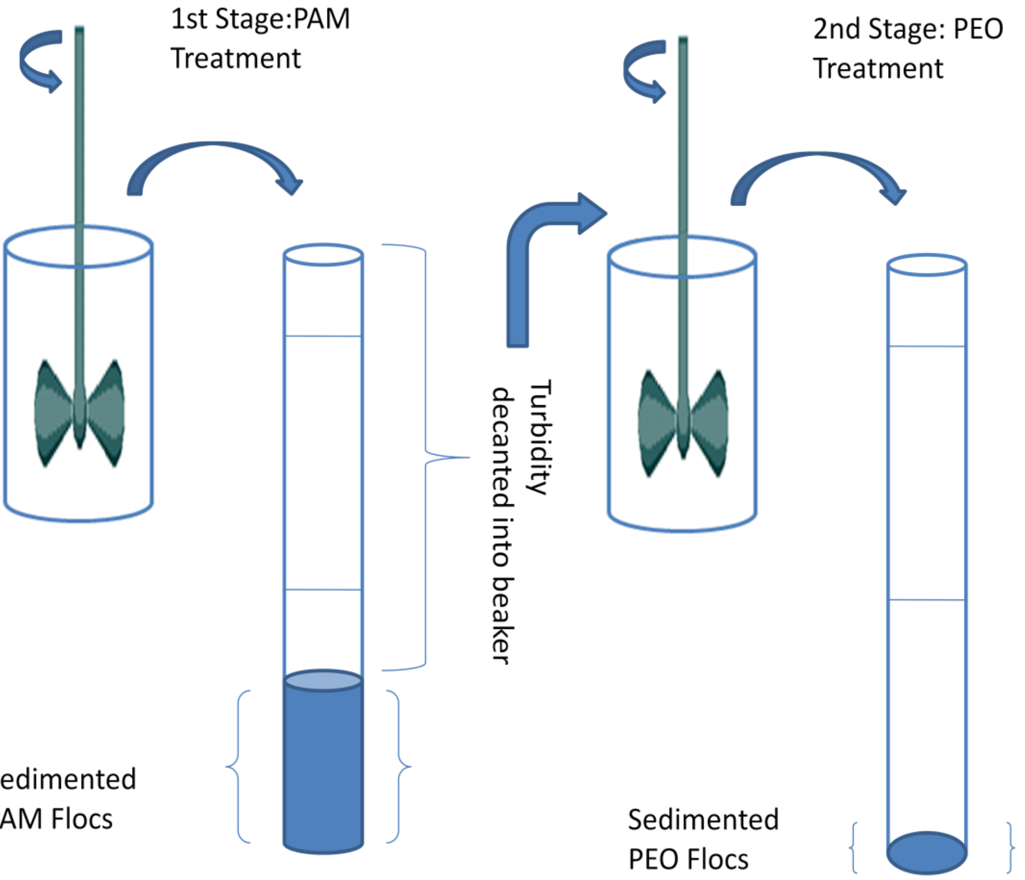


Figure 20. Two Staged Flocculation: 1) Polyacrylamide in the First Stage; 2) Polyethylene Oxide in the Second Stage

After first stage flocculation treatment was completed and turbidity measurements were done, the turbid supernatant of the suspension was decanted (Figure 20) into another 800 ml graduated beaker for the second stage flocculation using polyethylene oxide and following the same experimental procedure of the first stage flocculation.

$CaCl_2$ and $MgCl_2$ were added to the suspensions to define their effect on the flocculation of each clay type. $CaCl_2$ and $MgCl_2$ were obtained from the MERCK Chemicals. They were added at concentration of 100 mg / L, 250 mg / L and 500 mg / L in the pulp. Their influence on the clays flocculation tried to be identified according to the turbidity measurements by applying different dosages of UMA Magnafloc.

pH was also another important factor in the flocculation process. So, the pulp pH was decreased from original pH = 9.40 to neutral pH by using 1M HCl. After the pulp pH was adjusted, the flocculation studies were carried out at different dosages of UMA Magnafloc. Eventually, the results of the flocculation in the original and neutral pH conditions were compared with each other in terms of the NTU values.

The clay samples were also aged for 24 hours in distilled water and then the flocculation experiments were carried out with the aged samples to differentiate the behavioral change in the turbidity values after the aging period.

For the purpose of comparing new UMA Magnafloc performance with some other flocculant types (several polyacrylamides and polyethylene oxide), the suspensions were tried to be flocculated by adding the same dosages of each flocculant that ranges from nonionic charges to very high anionic charges. As a result, the UMA Magnafloc performance among the other flocculants and the effect of increasing anionic charge of the polymers on the flocculation of the clays were tried to be explained.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Sedimentation Behavior of the Clay Suspensions in Distilled Water and Tap Water

In order to have a baseline study on the differences between the settling behavior of the green and white clay samples, suspensions of the two clay samples were prepared by using either distilled water or tap water. These suspensions were subjected to gravitational sedimentation without flocculant addition for 24 hours.

Figure 21 shows the state of sedimentation of the suspensions after 24 hours, and Table 10 presents the turbidity measurements in the supernatants. Suspensions prepared with tap water settled to much smaller sediment volumes with relatively clearer supernatants, particularly in the case of the green clay sample. In distilled water, however, there was no significant settling; and, in fact, it remained as a stable suspension even after 1.5 months. Particularly, the green clay suspension in distilled water interestingly resulted in a striking turbidity of 23744 NTU at the end of 24-hour settlement period. This great turbidity may be originated from the mineralogical conditions of the green clay that was explained previously and characterized as rich in the swelling type mineral, montmorillonite.

Table 10. Turbidity and pH Measurements* of the Clay Suspensions in Distilled and Tap Water after 24 Hours

Distilled Water + Green Clay	**Distilled Water + White Clay**	**Tap Water + Green Clay**	**Tap Water + White Clay**
pH = 9.46	pH = 10.03	pH = 9.05	pH = 9.01
Turbidity = 23744 NTU	Turbidity =7062 NTU	Turbidity = 10 NTU	Turbidity = 134 NTU

* Measurements were carried out after 24 hours of settling period.

Figure 21. Sedimentation Behavior of the Suspensions (3% Clay; After 24 Hours)

4.2 Flocculation of the Clay Suspensions

The montmorillonite-rich green clay and dolomite-rich white clay suspensions were flocculated (in distilled water which consists of 3% clay by weight) by different dosages of 0.01% UMA Magnafloc with 3% borax availability. The turbidity results of experiments were plotted in terms of NTU against polymer dosage (Figure 22). It was observed in the Figure 22 that 0 – 1000 gr per ton polymer dosages had a slope which results in decreasing turbidity of supernatant with increasing dosage amount but for polymer dosages above the 1000 gr per ton, flocculation ability of UMA Magnafloc was fixed down to 1000 NTU for the green clay suspension and down to 700 NTU for the white clay suspension; turbidity could not be eliminated by increasing the dosage.

The high turbidity results of the clay suspensions may be explained with zeta potential of the particles. The zeta potential of the particles was measured as – 41.20 mV (– 47.60 mV in the presence of borax) for the green clay and – 33.50 mV (- 37.40 mV in the presence of borax) for the white clay at original suspension pH (Figure 18). Relatively good flocculation performance of the white clay particles may be explained with this difference in zeta potentials of the clay samples. It seems that the UMA Magnafloc is slightly more effective on the white clay suspension than the green clay under same conditions (pH = 9.4). This high zeta potentials probably deteriorated flocculation of the clay suspension. Kuz'kin and Nebera (1966) also stated that similarly there was a sharp deterioration in the flocculation performance of anionic polyacrylamide at high pH values and there were observed no improvement with different (anionic) polyacrylamide treatments. This was explained by them with very intense reduction in the adsorption of the reagent on a negatively charged surface of clay particle that had a zeta potential greater than – 40 mV. Briefly, they defined the zeta potential of – 40 mV as first breaking point where flocculation was obscured and – 60 mV as a second breaking point where flocculation became impossible with polyacrylamide type polymers. Challenge in the flocculation of the clay suspensions may arise from this surface phenomenon.

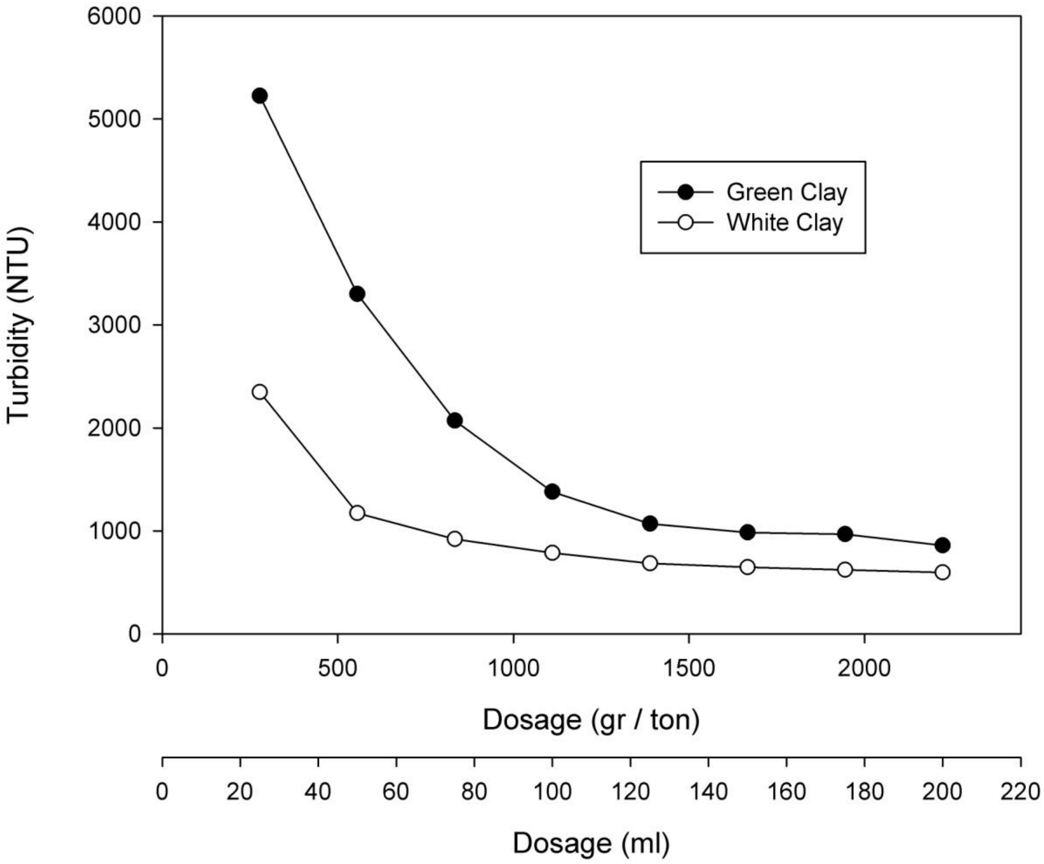


Figure 22. First Stage Flocculation of the Clay Suspensions
with UMA Magnafloc (3% Clay; 3% Borax; pH = 9.40)

The turbid supernatant of the green clay flocculation with UMA Magnafloc (at dosage = 100 ml) was decanted to another beaker for the second stage flocculation and treated with different type polymer, non-ionic polyethylene oxide. Figure 23 shows second step flocculation performance of both clay samples against polyethylene oxide dosage. Up to 50 ml polymer dosage curve seems to be very steep but the slope decreased slightly above 50 ml. The turbidity level decreased down to 32 NTU with 100 ml polymer addition.

Similar to the green clay flocculation, the turbid supernatant of the white clay flocculation with UMA Magnafloc could not remove the turbidity, completely. So, the turbid supernatant of the white clay flocculation with UMA Magnafloc (at dosage = 100 ml) was decanted to another beaker for the second stage flocculation with non-ionic polyethylene oxide. Dosage studies (Figure 23) showed that the turbidity removed easily with 25 ml polyethylene oxide down to 34 NTU and down to 10 NTU with 50 ml polymer addition successfully.

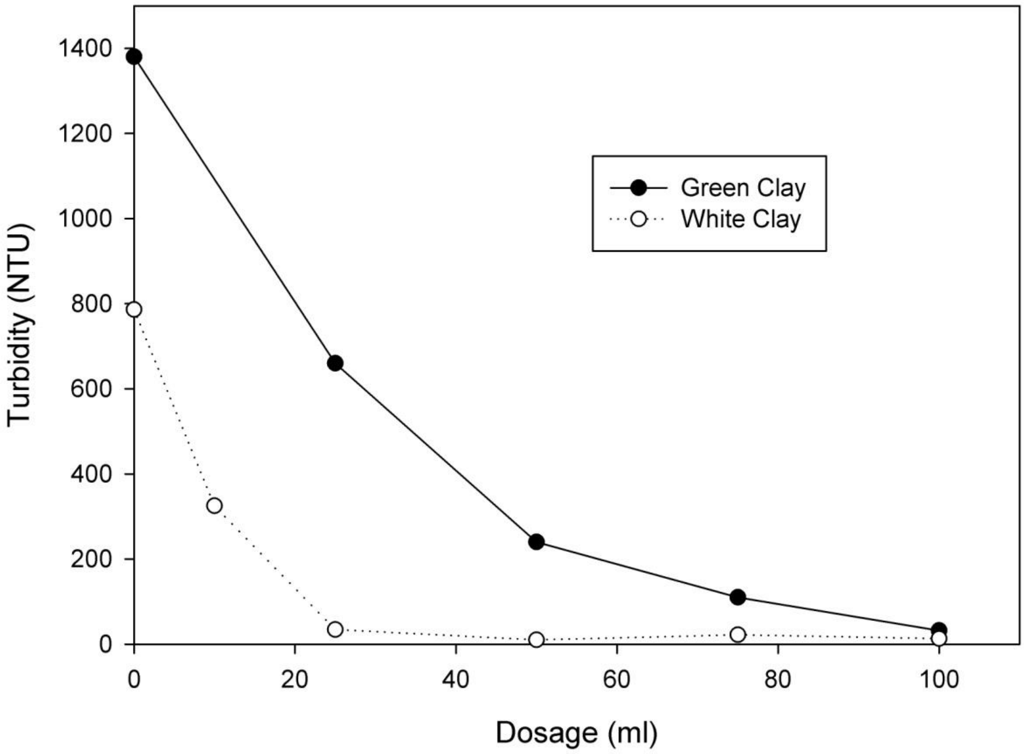


Figure 23. Second Stage Flocculation of the Clay Suspensions with Polyethylene Oxide (pH = 9.40)

As a result of two-stage flocculation studies, it was observed that the polymeric flocculant consumption range was very high for both clay suspensions. The previous works (Sabah and Yesilkaya, 2000; Yüksel and Kurama, 2009) also studied this type of Kırka clay tailings and their dosage works were in the same high range. Moreover, Sabah and Yesilkaya (2000) stated that the Kırka plant’s actual flocculant consumption is also between 1000 gr / ton and 1500 gr / ton.

In conclusion, consecutive double flocculants addition seems to be very effective in terms of turbidity removal in distilled water because performance of the UMA Magnafloc seems to be decreased at very high dosages, it can be said that consecutive flocculation process with relatively low dosages of polymers addition at each stages enhances the process.

4.3 Effect of Borax on the Flocculation of the Clay Suspensions

The flocculation behavior of the clay suspensions was studied with borax concentrations of 3%, 10% and 15%. The clay content was fixed at 3% throughout the borax effect experiments.

Figure 24 clearly indicates that increasing the borax concentration has a positive effect in the flocculation of the green clay suspension. For instance, by adding 200 ml polymer solution, the turbidity values were measured as 860 NTU with 3 % borax content, 480 NTU with 10 % borax content and 398 NTU with 15 % borax content. As a result of the experiments, it can be concluded that both dosage and turbidity decreased by increasing borax percentage.

Similarly, the borax effect was also experimented for the flocculation of the white clay suspensions. It was observed (Figure 25) that increased borax addition resulted in improved flocculation of the dolomite-rich white clay suspensions. For example, by adding 200 ml polymer solution, the turbidity values were measured as 597 NTU with 3 % borax, 345 NTU with 10 % borax and 210 NTU with 15 % borax.

Borax is a very soluble substance. Once it is dissolved, it causes change in the surface charge of silicates and carbonates by adsorbing on it (Keren et al., 1994) and does change the dissolution characteristics and dissolution rate of the carbonates (Goldberg, 1997; Kosmulski, 2009; Gür et al., 1994). The zeta potential measurements showed that borax presence makes the surface of both clay samples more negatively charged (Figure 18). This was rather interesting because the flocculation using anionic type polymer was enhanced although the zeta potential of both clay samples became more negative (from –41.20 mV down to –47.60 mV for the green clay and –33.50 mV down to – 37.50 mV for the white clay) in the presence of borax. When the previous studies were considered related to the borax effect on the flocculation performance, some contradictions emerged between the researchers (Gür et al., 1994; Sabah and Yesilkaya, 2000; Goldberg, 1997) and the mechanism could not be explained exactly. In spite of the contradictions, the clear results were obtained that increasing borax concentration slightly improved the flocculation process of the clay suspensions and the turbidity values in this study.

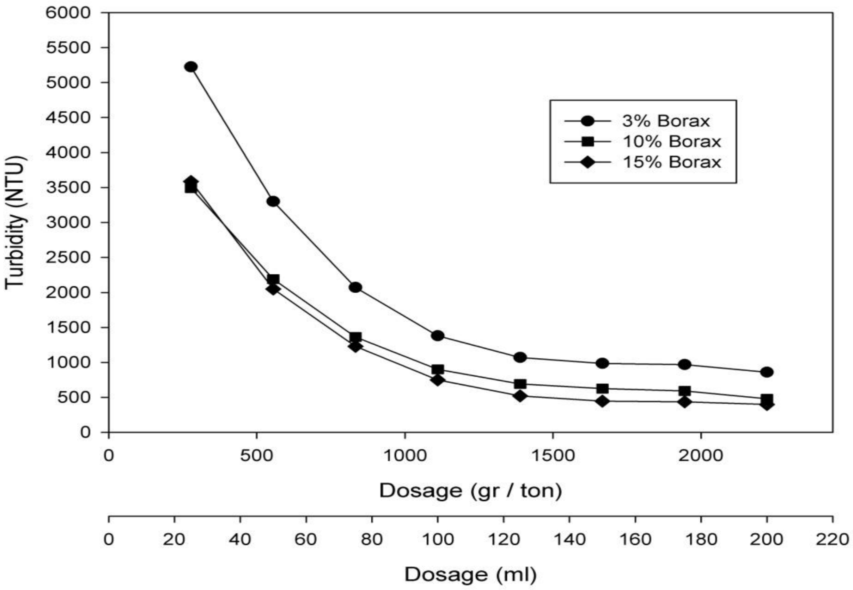


Figure 24. Effect of Borax on the Flocculation of the Green Clay Suspension

(UMA Magnafloc; 3% Clay; pH=9.40)

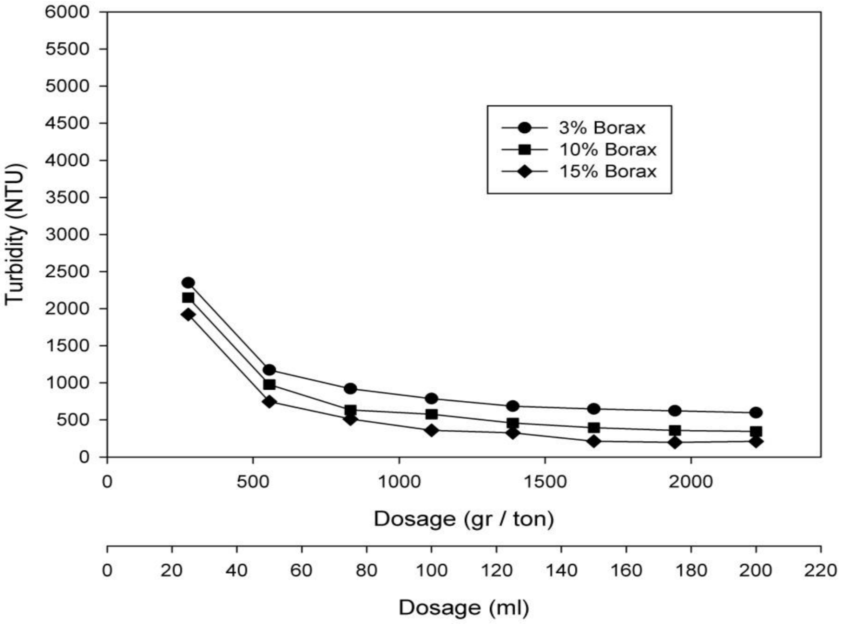


Figure 25. Effect of Borax on the Flocculation of the White Clay Suspension

(UMA Magnafloc; 3% Clay; pH=9.40)

4.4 Effect of Solid/Liquid Ratio on the Flocculation of the Clay Suspensions

Solid / liquid ratio effect on the flocculation of the green clay suspension was studied with initial solid content of 3%, 10% and 15%. The results of these experiments were plotted on Figure 26 and Figure 27 (dilution due to the polymer addition is ignored).

Flocculation performance of the green clay suspension drastically changed with the amount of solid in the suspension. For example, the turbidity was 1380 NTU with (initial) 3% solid amount after around 1000 g/ton flocculant was used but this value significantly increased to 3160 NTU with (initial) 10% solid amount and 4550 NTU with (initial) 15 % solid content. So, low solid / liquid ratios can be defined as a favorable parameter for the flocculation of the green clay suspension as shown in Figure 26.

Low Solid / liquid ratio was proved as a favorable parameter for the flocculation of the white clay suspension similar to the green clay suspension. For example, by using around 1000 gr/ton flocculant, the turbidity results of the flocculation of the white clay suspension were found as 786 NTU, 1038 NTU and 1226 NTU with respect to (initial) 3%, 10% and 15% solid content. So, increasing solid amount decreased flocculation performance significantly as shown in Figure 27.

The past studies showed that flocculation process may be enhanced by diluting samples because adsorption densities of polymers (adsorbed polymers amount per gram of solid) sharply decreased (Kurşun et al., 2000) while solid concentration increased. In addition to that, the probability of polymer-particle collision may increase in the low solid / liquid ratio suspension. In such a diluted system, this increased interaction of the polymer and particles may result in enhanced flocculation and lower turbidity values.

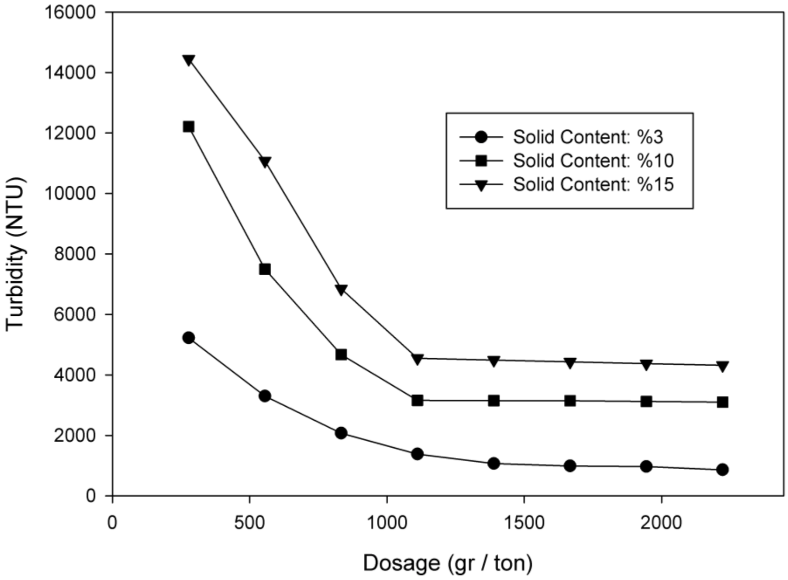


Figure 26. Effect of Solid/Liquid Ratio on the Flocculation of the Green Clay Suspension (UMA Magnafloc; 3% Borax; pH = 9.40)

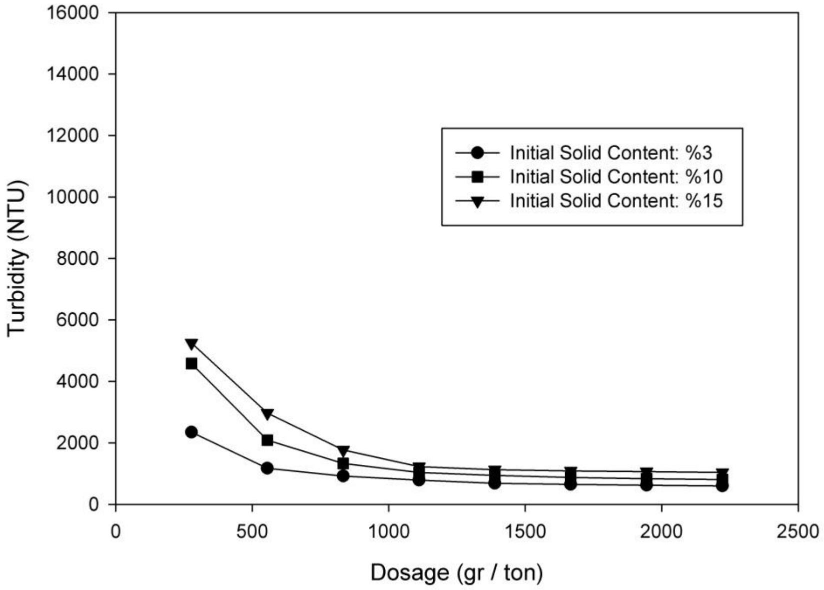


Figure 27. Effect of Solid/Liquid Ratio on the Flocculation of the White Clay Suspension (UMA Magnafloc; 3% Borax; pH=9.40)

4.5 Effect of $CaCl_2$ on the Flocculation of the Clay Suspensions

The clay minerals generally have high adsorption capacity for the cations (Somasundaran & Hubbard, 2004). According to Somasundaran and Hubbard (2004), cations have a different adsorption amount on clay materials and they claim that Ca^{++} is the most effectively adsorbed species on the surface of clay minerals and adsorption amount decreases from Ca to Zn according to this sequence, Ca > Pb > Cu > Mg > Cd > Zn. Pb, Cu, Cd and Zn were economically infeasible and may cause to environmental problems. So, the flocculation behavior of the clay suspensions was experimented with different $CaCl_2$ concentrations of 100 mg/L, 250 mg/L and 500 mg/L (The amount of the clay was fixed to 3 %).

The results of the flocculation tests were plotted as shown in Figure 29 and Figure 30. Calcium ions significantly improved the flocculation of the green clay suspension. Turbidity of the green clay suspension decreased down to 6 NTU with 500 mg $CaCl_2$ / L and UMA Magnafloc. $CaCl_2$ was proved as a very effective also for the flocculation of the white clay suspension. The white clay suspension flocculated successfully down to 28 NTU with the help of 500 mg $CaCl_2$/L. Furthermore, polymer consumption decreased for both clay suspensions by increasing Ca^{++} amount. When flocculation performances of the suspensions were compared, $CaCl_2$ seems more effective on the green clay than the white clay at 500 mg $CaCl_2$ /L.

Upon Ca^{++} ions addition, calcium formed a metal-hydroxo complex species ($CaOH^+$) (Morris & Zbik, 2009) and this species subjected to rapid adsorption on both edge and basal surfaces of montmorillonite. So, most probably the active sites on the particles were increased due to adsorbed calcium and polymers easily attached themselves on those active groups. This clay surface – Ca^{++} – polymer interaction was tried to be illustrated as shown in Figure 28.

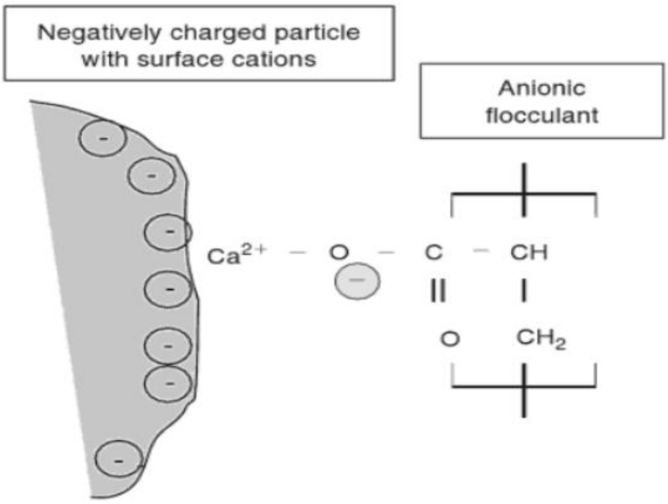


Figure 28. Calcium Adsorbed Suspended Clay Particle Interaction with Anionic Flocculant (Williams, 2007)

As explained previously, this Ca adsorption significantly increased flocculation. Polymers can attach themselves on the isolated groups of (MeOH) and (SiOH) with hydrogen bonding mechanism (Mathur & Moudgil, 1997). In the case of calcium hydroxo-complex species availability on the surface of particles, polymers hold on to these active sites leading to more stable and stronger floc formations. This phenomenon was stated by several authors that polymeric flocculant (especially negatively charged flocculants) may form stronger chemical bonds in the presence of Ca^{++} ions (Stutzman and Siffert, 1997; Alptekin, 2006). In addition, anionic polymers were in the best condition in terms of the stretched conformation at pH 9.40. Their elongated tails easily entrapped other suspended particles in the solution by enhanced bridging mechanism and the electrostatic interaction also promoted with the help of the Ca^{++} charge neutralization property on the surface of clay particles. Consequently, very good flocculation performances with very low flocculant consumption and very low turbidities were reached with 500 mg $CaCl_2$ / L and also very strong flocs (pellet like) were formed especially for montmorillonite-rich green clay suspensions.

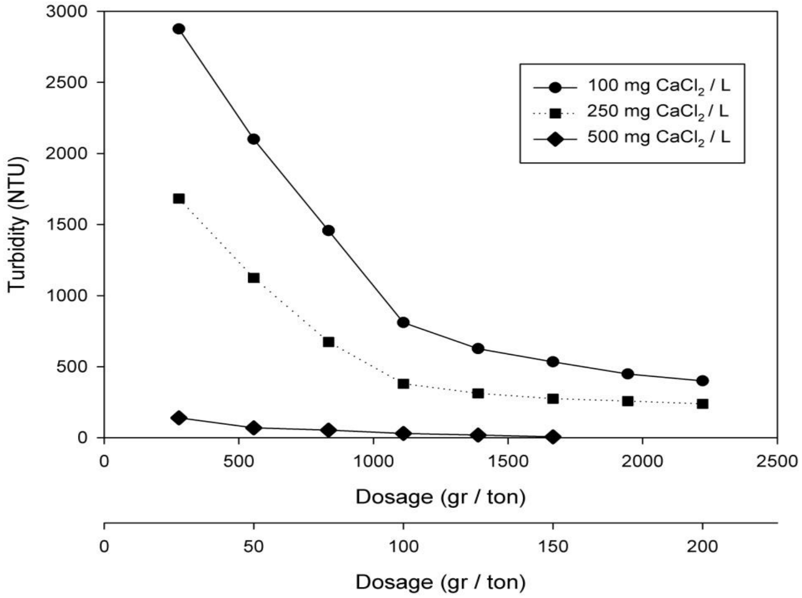


Figure 29. $CaCl_2$ Effect on the Flocculation of the Green Clay Suspension (UMA Magnafloc; 3% Clay; 3% Borax; pH = 9.40)

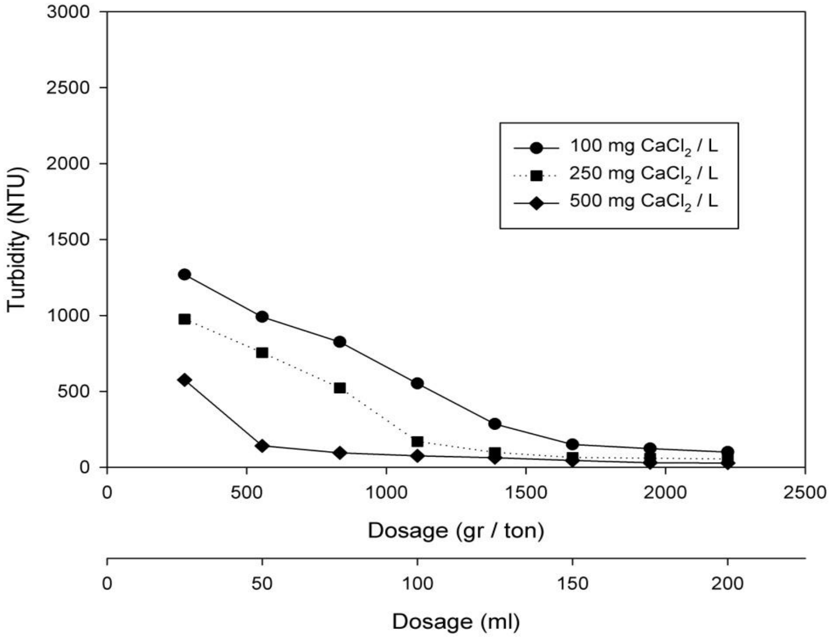


Figure 30. $CaCl_2$ Effect on the Flocculation of the White Clay Suspension (UMA Magnafloc; 3% Clay; 3% Borax; pH = 9.40)

Calcium was proved as a useful cation that enhances flocculation significantly in terms of turbidities and polymer consumption as previously experimented. In addition to that, there is another beneficial feature of calcium on the flocculation. Figure 31 and Figure 32 revealed the floc formations with the concentration of 500 mg $CaCl_2$ / L (on the right hand side) and 100 mg $CaCl_2$ / L (on the left hand side). Especially, montmorillonite-rich green clay samples flocculated with Ca^{++} gave very strong flocs, which can be detected easily by the naked eye. Moreover, again Ca^{++} treated green clay flocs were much denser. Whereas the sediments volume of 100 mg / L and UMA Magnafloc was 125 ml, final sediment volume of 500 mg / L Ca^{++} and UMA Magnafloc was decreased down to 90 ml. Also, the size of the flocs increased with increasing Ca^{++} availability in the suspension. This property of UMA Magnafloc flocculation with calcium addition will ease the further possible filtration processes for swelling type clay samples in other industries because the green clay flocs treated with 500 mg / L $CaCl_2$ can be screened easily even by using a sieve with 1–mm aperture size. On the other hand, it was very interesting that the same Ca^{++} amount was experimented with dolomite-rich clay samples under the same conditions and no significant differences were observed on the flocs structure between the 100 mg/L and 500 mg/L of Ca^{++} (Figure 32). When two clay samples were considered, the flocculated white clay sample had much denser final structure than the green clay did. This most probably stemmed from swelling property of the montmorillonite mineral in the green clay and it was very normal that the swelled mineral resulted in less dense flocs due to the increase in the sediment volume.

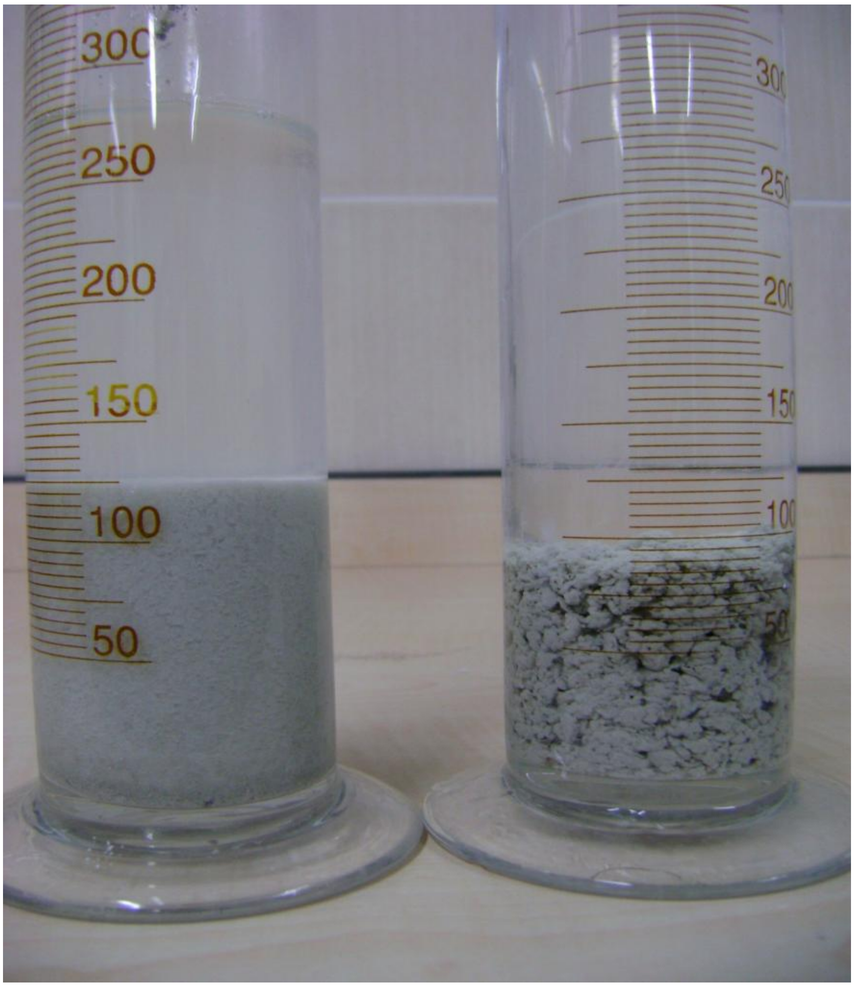


Figure 31. The Green Clay Flocs at Calcium Concentration: 100 mg / L on the left side and 500 mg / L on the right side (3% Borax; 3% Clay; 100 ml-UMA Magnafloc as Flocculant; pH=9.40)

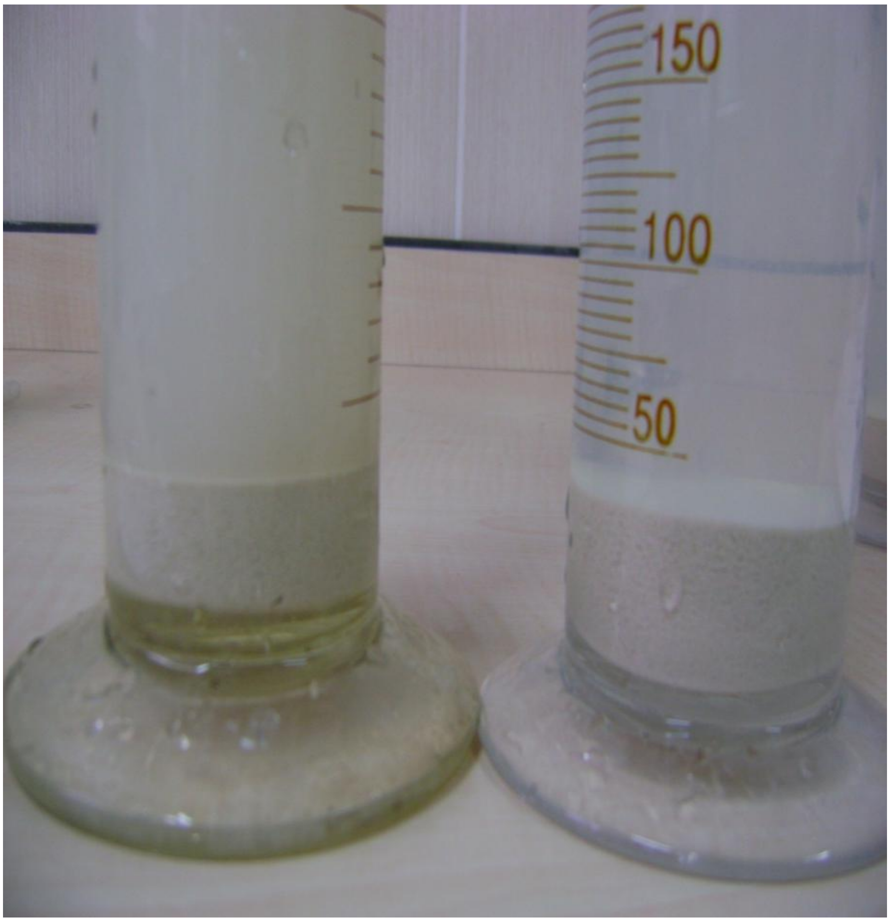


Figure 32. The White Clay Flocs at Calcium Concentration: 100 mg / L on the left side and 500 mg / L on the right side (3% Borax; 3% Clay; 100 ml-UMA Magnafloc as flocculant; pH=9.40)

4.6 Effect of $MgCl_2$ on the Flocculation of the Clay Suspensions

$MgCl_2$ effect on the flocculation of the clay suspensions was studied with the dosage of 100 mg/L, 250 mg/L and 500 mg/L (The amount of the clay was fixed to 3 %). The results of these experiments were plotted on Figure 33 and Figure 34.

Increasing $MgCl_2$ amount resulted in slight enhancement of the flocculation of the green clay suspension but the turbidity removal was very limited as shown in Figure 33. Even, it can be said that Mg was inefficient particularly compared to Ca ion in terms of the flocculation process. For instance, the turbidity decreased down to 1244 NTU in the presence of the 500 mg $MgCl_2$/L despite approximately 1000 g/ton UMA Magnafloc polymer was added to the suspension. Magnesium seems to be unfavorable flocculant aid for the flocculation of the green clay suspension.

Similar study was carried out for the white clay suspension but $MgCl_2$ showed a deteriorating effect for the flocculation of the white clay. Increasing $MgCl_2$ from 100 mg / L to 500 mg / L resulted in increasing turbidity and flocculation performance decreased (Figure 34). The adverse effect of magnesium ion was not clearly indicated in terms of the flocculation in mineral processing but this adverse effect is well known in soil science especially for erosion and irrigation studies. The past studies (Singh, 2005) clearly indicated that magnesium-rich aqueous solutions led to the dispersion of clays and behaved in a very different way when compared to calcium-rich solutions. Similarly, Soil Resources Division of United States (1993) and Abrol (1988) fell into line with Singh by claiming that magnesium fosters the dispersion of fine clayey materials. Abrol (1988) stated that magnesium had a specific role in the hydraulic conductivity loss of the clays. Agassi (1996) also agreed that magnesium decreased the permeability of the soil layer due to the disperison. Based on these explanations, dolomite mineral was pointed as main Mg source in the soil formations and proved to be responsible from surface runoff and erosion in the soil science due to its dispersive character on the clay formations (Dontsova and Norton, 1999).

Another interesting point about magnesium was underlined by Goyal (2003):

> “The hydrated Magnesium ion present in water is larger than hydrated Calcium, which decreases the linkages between external surfaces within clay aggregates, increasing the tendency for aggregate breakdown and clay dispersion” (p. 139).

In 2004, Donstova and the coworkers confirmed this inference of Goyal and stated that flocculation can be deteriorated due to the blockage of the external surfaces of the clay particles. The mentioned limitation of the linkages or blockage of the clay surfaces may include the polymer - clay interaction. This may be the reason of decreasing flocculation performance of the white clay suspension with increasing $MgCl_2$ amount.

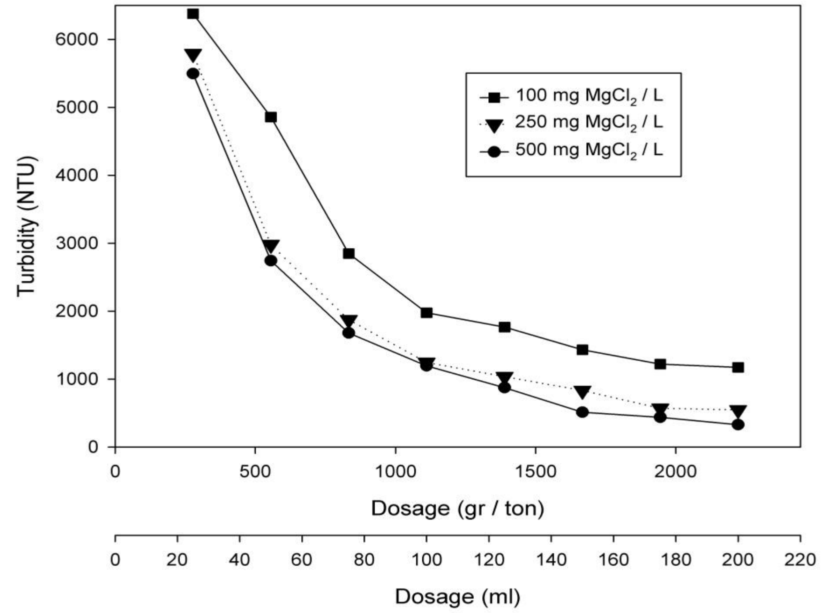


Figure 33. $MgCl_2$ Effect on the Flocculation of the Green Clay Suspension (UMA Magnafloc; 3% Clay; 3% Borax; pH = 9.40)

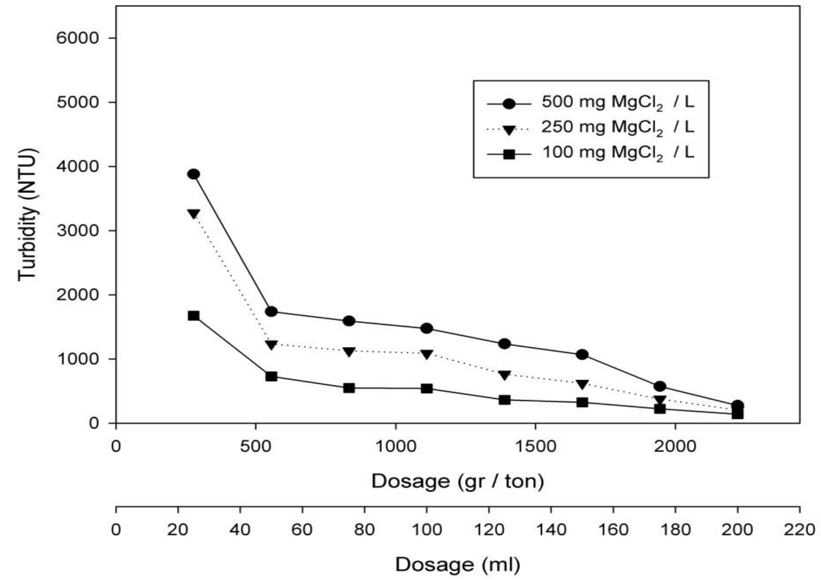


Figure 34. $MgCl_2$ Effect on the Flocculation of the White Clay Suspension (UMA Magnafloc; 3% Clay; 3% Borax; pH = 9.40)

4.7 Effect of Simultaneous $CaCl_2$ and $MgCl_2$ Addition on the Flocculation of the Clay Suspensions

Previous experiments showed that magnesium is an unfavorable agent for the flocculation of green clay suspension and deteriorating agent for the flocculation of the white clay suspension. Similar results were obtained for the flocculation of the green clay and the white clay suspensions when $CaCl_2$ and $MgCl_2$ were simultaneously added to these suspensions. The calcium favorable effect on the flocculation was deteriorated by magnesium adverse effect. As shown in Figure 35 and Figure 36, although equal amount of $CaCl_2$ (250 mg/L) and $MgCl_2$ (250 mg/L) added simultaneously to the suspensions, the flocculation performance was decreased by giving greater turbidity results when it was compared to only (250 mg/L) $CaCl_2$ added flocculation tests. Furthermore, $CaCl_2$ and $MgCl_2$ individual flocculation curves compared with each other, significant enhancement in turbidity removal was differentiated in calcium availability rather than magnesium.

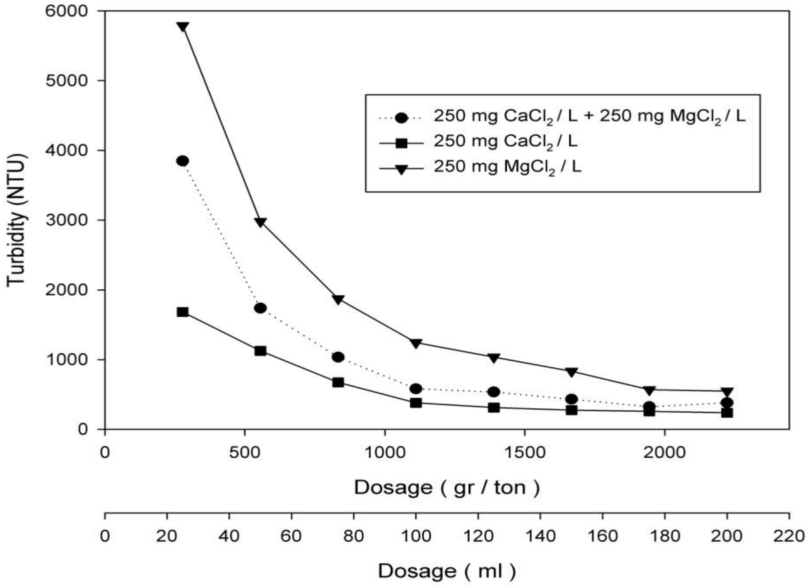


Figure 35. $CaCl_2$ and $MgCl_2$ Effect on the Flocculation of the Green Clay Suspension (UMA Magnafloc; 3% Clay; 3% Borax; pH=9.40)

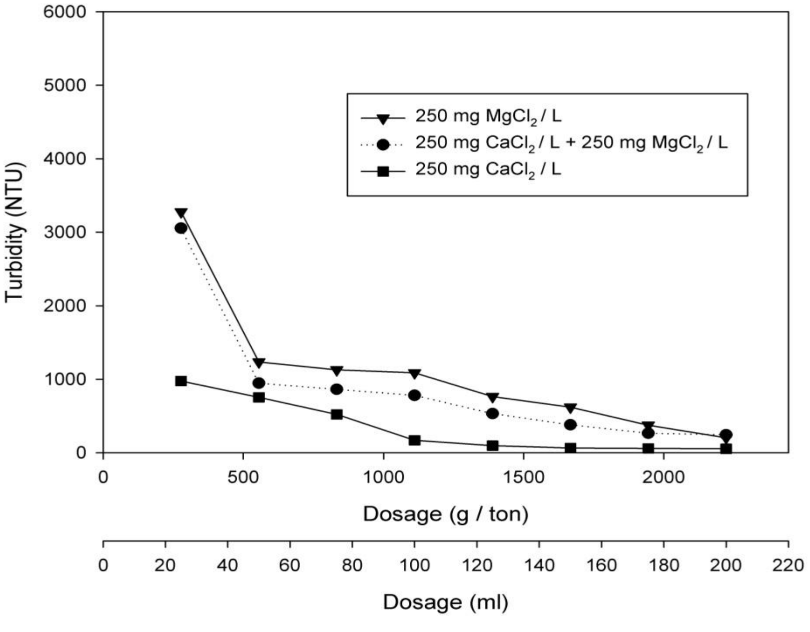


Figure 36. $CaCl_2$ and $MgCl_2$ Effect on the Flocculation of the White Clay Suspension (UMA Magnafloc; 3% Clay; 3% Borax; pH=9.40)

Donstova and Norton (1999) claimed that the main magnesium source in the clayey material and soil was dolomite or dolomitic limestones in nature and Mg from dolomitic formations caused to the dispersion of clays. They also studied Ca and Mg relation on the sedimentation of clays and they observed that calcium treated clay samples easily flocculated (Although they prefer “flocculation”, maybe the process should be named as coagulation or sedimentation). The clay samples became dispersed by adding and increasing Mg amounts at varying Ca:Mg ratios and at 0:100 of Ca:Mg ratio, the clay stability was increased and it became fully dispersed.

4.8 Effect of pH on the Flocculation of the Clay Suspensions

The original borax tailings pH was stated to be around 9.3 – 9.4 by some previous researchers (Kozulu, 2003; Sabah & Yesilkaya, 2000; Garrett, 1998; Khan, 1980). The prepared clay suspensions showed similar pH characteristics due to borax addition that acts as buffer. This pH of the borax-clay suspensions was preserved even after polymeric flocculant added into the system and there was no pH variation observed during the experiments (Figure 37). The adverse effect of this kind of pH fixation was stated by Stechemesser and Dobias (2005). They claimed that there may be a difference in flocculation behavior between fixed and variable pH conditions and flocculation performance can be affected under fixed pH conditions.

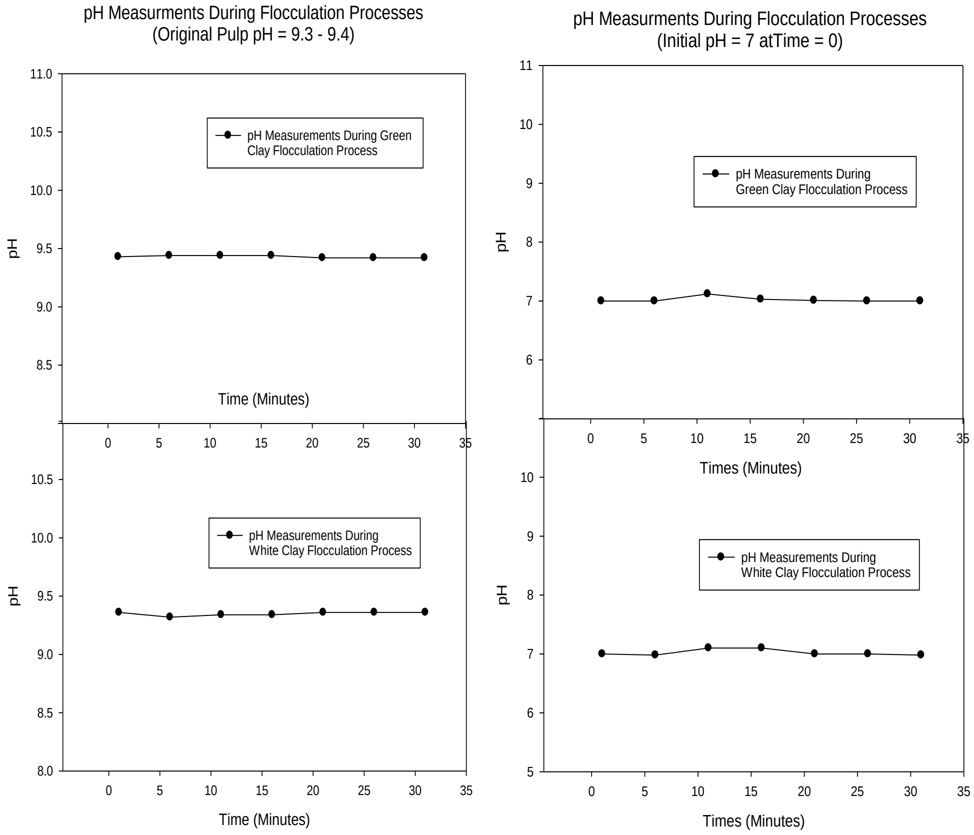


Figure 37.pH Measurements during Flocculation at Original pH 9.40 and Adjusted pH 7.00

Polyacrylamide based flocculants are sensitive to pH variations. At low pH values, the macromolecules coil up and they do not adsorb on the particles or cause high polymer consumption. This coiled up state of polymers can be changed by adjusting pH. Increasing pH causes elongation of macromolecules through solution and they have stretch conformation (Figure 38) at around pH 9. That stretched conformation is very important because bridging mechanism is fully activated and flocculation performance increases due to available active polymer segments (Lu et al., 2005) increase for the purpose of adsorption on clay particles. Although the original pH of the prepared green and white clay suspensions is very suitable for flocculation (when conformation of polymeric macromolecules is considered), there is another aspect of flocculation, negatively charged clay surfaces. The performance of the polyacrylamide on clay suspensions, especially anionic polyacrylamides, decreases at high pH because the surface charge of particles become more negative and repulsion takes place between polyacrylamide and negatively charged particles (Stechemesser and Dobias, 2005). As a result, the optimum flocculation pH was defined by many authors as around neutral pH 7 (Vargas, 2007; Stechemesser and Dobias, 2005) for the flocculation of the clay suspensions with polyacrylamide type flocculants. So, UMA Magnafloc was tested under neutral pH condition for the purpose of performance comparison.

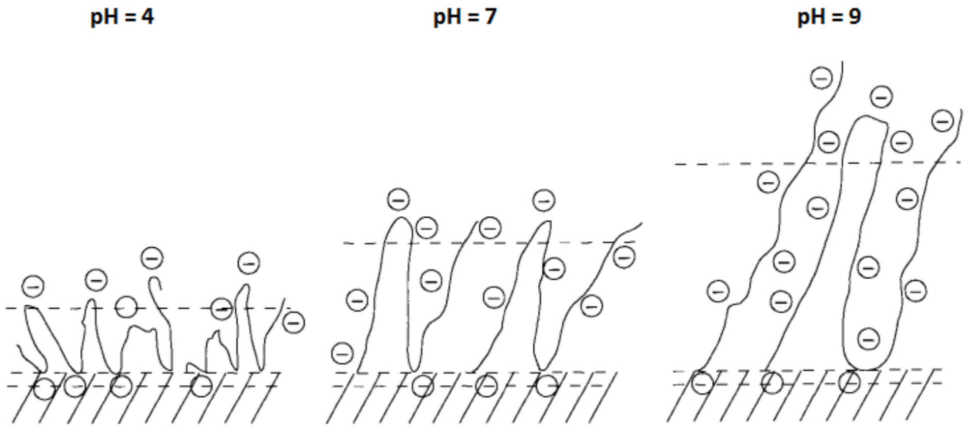


Figure 38. Conformational State of Polymer According to pH (Lu et. al. 2005)

The results of flocculation experiments under neutral pH were shown in Figure 39. It was interesting that the mineralogical differences of two clay samples vanished in terms of flocculation behavior and the character of turbidity – dosage curves became very similar to each other. This statement can be explained by increased performance and adsorption of polymers that dominated the surface differences of two clay types.

Another interesting point was the polymer consumption. The consumption was significantly reduced when it was compared to the flocculation results under original pH conditions. The very high flocculant consumption (for both experimental studies and actual industrial application of the Kırka Plant) reason was explained with high surface area of very fine clay particles that leads to high polymer adsorption on the surface (Sabah and Yesilkaya, 2000) but the consumption amount was decreased with pH adjustment and Figure 39 proved that the particle size was not a primary concern in the flocculation of the clays of Kırka Region.

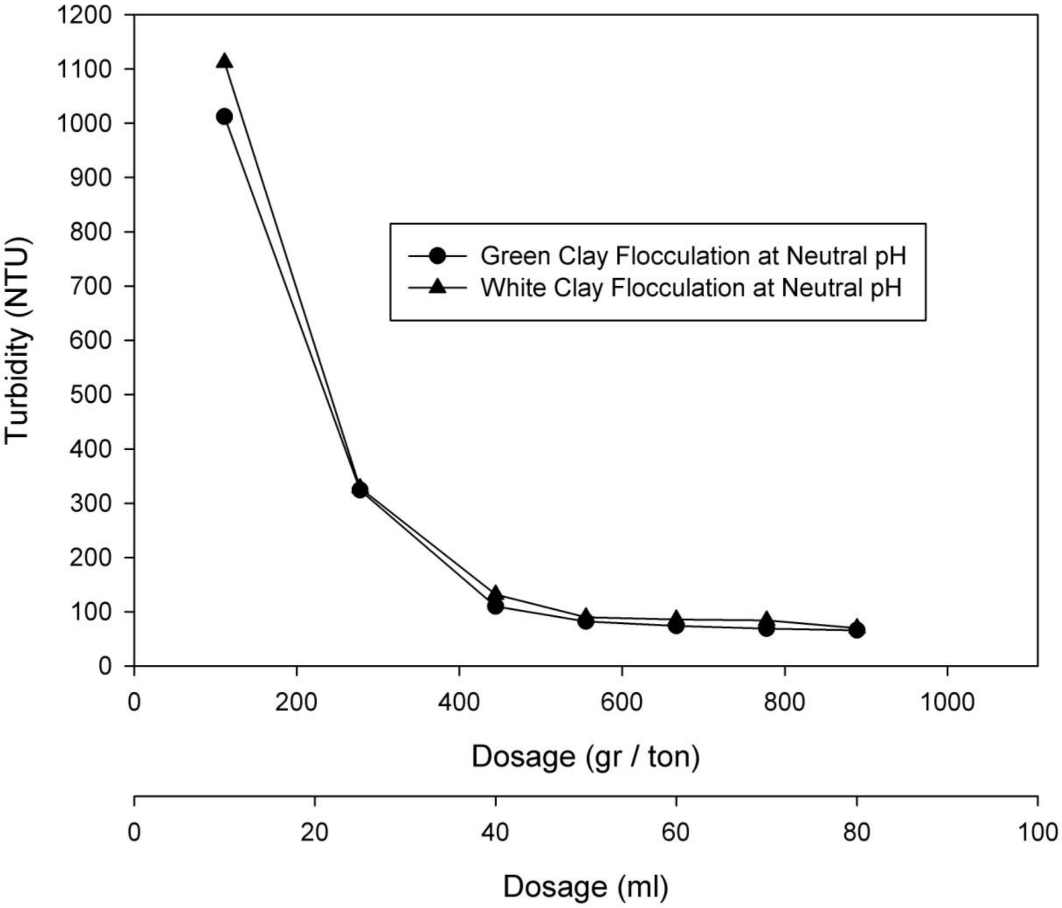


Figure 39. Flocculation Behavior of the Clay Suspensions at Adjusted pH 7.00 (UMA Magnafloc; 3% Clay; 3% Borax)

The turbidity of 40 ml UMA Magnafloc flocculation tests decanted into another beaker and treated with 10 ml polyethyleneoxide. Similar results (Table 11) were also obtained for two clay types at this second stage flocculation. The turbidity decreased down to around 6 – 7 NTU. As a result, polyethylene oxide was proved as a useful macromolecular polymer for the purpose of removal of the supernatant turbidities.

Table 11. Turbidity Values after Second Stage Flocculation with PEO (pH = 9.40)

The turbidity of 40 ml UMA treatment decanted and re-treated with PEO	**Turbidity of green clay**	**Turbidity of white clay**
Initial turbidity	110	132
10 ml %0.01 PEO addition (10 minutes of mixing period)	6.2	6.8

After flocculation processes were completed, solid amounts in the turbidities (suspended particles that could not be flocculated with UMA Magnafloc flocculation) at original and neutral pH were filtered through with 0.4 micron aperture size filter paper. After the filter papers were completely dried, the weight of clay samples were calculated and plotted in Table 12. As it was stated previously, flocculation was relatively easy at pH 7 than the original pH of pulp. Around ninety-nine percent by weight of both clay samples were flocculated at pH 7 but, these percentages (by weight) were decreased down to 67.5% for the green clay and 92.94% for white clay suspensions at the original pH (9.40).

Table 12 Comparison of Flocculation Performance at Neutral and Original pH According to Solid Amount Flocculated

Comparison of Flocculation Performance in terms of Solid Amount	**Solid Amount in the Turbidity of Green Clay Flocculation with UMA Magnafloc**	**Solid Amount in the Turbidity of White Clay Flocculation with UMA Magnafloc**
Original pH = 9.3 – 9.4	2.925 g. (67.5% of Solid Flocculated)	0.635 g. (92.94% of Solid Flocculated)
Neutral pH = 7	0.087 g. (99.03% of Solid Flocculated)	0.081 g. (99.10% of Solid Flocculated)

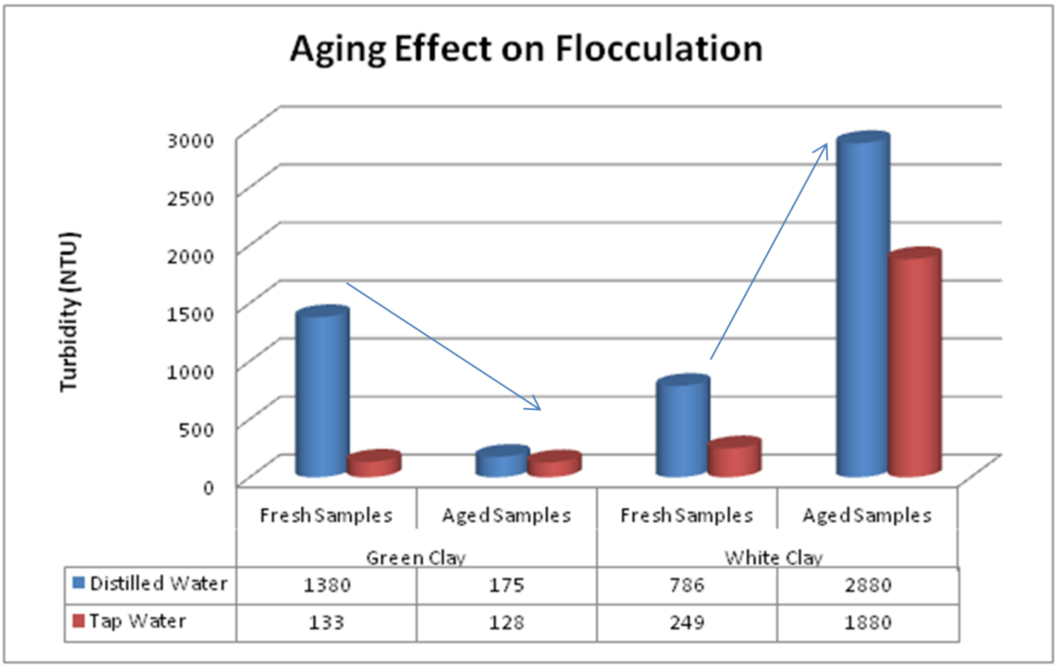
In conclusion, the pH adjustment seems to be very efficient parameter in flocculation of the clay suspensions but borax in the actual tailings causes some problem for the industrial application of this parameter. As mentioned previously, borax mineral buffers the solution and fix pH. So, adjustment of the pulp pH is very challenging and maybe uneconomic in terms of the acid consumption. For the purpose of comparison of acid consumptions in the presence and absence of borax, the consumption tests were carried out to reveal the differences. To do this, 1 M hydrochloric acid was used and consumption amounts plotted on Table 13 in terms of millimeter for each clay type. The outcomes showed that borax availability resulted in very high acid consumption. As it seen clearly below, borax availability increased HCl consumption 12 – 14 times greater than the clay only samples and it seems to be inconvenient to adjust pH for the flocculation in the actual plant conditions.

Table 13 HCl Consumption to Adjust pH of the Clayey Pulps

Hydrochloric Acid (1 M) Consumption Required to Adjust pH to 7.00		
Clay Type	%3 Borax + 300 ml Distilled Water	Distilled Water Only (No Borax Addition)
Green Clay	43.60 ml	3.70 ml
White Clay	43.50 ml	3.10 ml

4.9 Effect of Aging on the Flocculation of the Clay Suspensions

The clay samples were aged for a period of 24 hours in both distilled water and tap water for the purpose of determining any possible change in the flocculation behavior due to the surface alteration of silicate minerals and especially soluble carbonate minerals. The tests showed (Figure 40) different results for the clay samples although the dosage was fixed during the experiments. Flocculation of the green clay suspension resulted in much lower turbidity values down to 175 NTU (in distilled water) and 128 NTU (in tap water) when it was aged for one day. It can be said that aging has a positive effect on the flocculation of the green clay suspension. The reason of that may be explained by increasing amount of the isolated – OH groups that enhances the adsorption of polymers on clay surfaces during aging period (Somasundaran and Hubbard, 2004). In contradiction to the green clay suspension, the flocculation of the white clay became difficult and turbidity values increased up to 2880 NTU (in distilled water) and 1880 NTU (in tap water) after aging period. The negative effect of aging on flocculation of dolomite may be explained by decreasing amount of the surface hydroxyl groups because Moudgil and Behl (1993) proved that the flocculation of the dolomite minerals became impossible when the isolated – OH groups removed from the mineral surfaces. This free OH groups have a crucial importance in terms of the polymer – clay surface interaction because isolated – OH groups on mineral surface acts like specific active chemical sites and these active sites proved to be responsible from the adsorption of the polymeric macromolecules (Rubio and Kitchener, 1976).



	Green Clay		White Clay	
	Fresh Samples	Aged Samples	Fresh Samples	Aged Samples
🟦 Distilled Water	1380	175	786	2880
🟥 Tap Water	133	128	249	1880

Figure 40. Aging Effect on the Flocculation of the Clay Suspensions (100 ml-UMA Magnafloc;3%Clay; 3% Borax; pH=9.40)

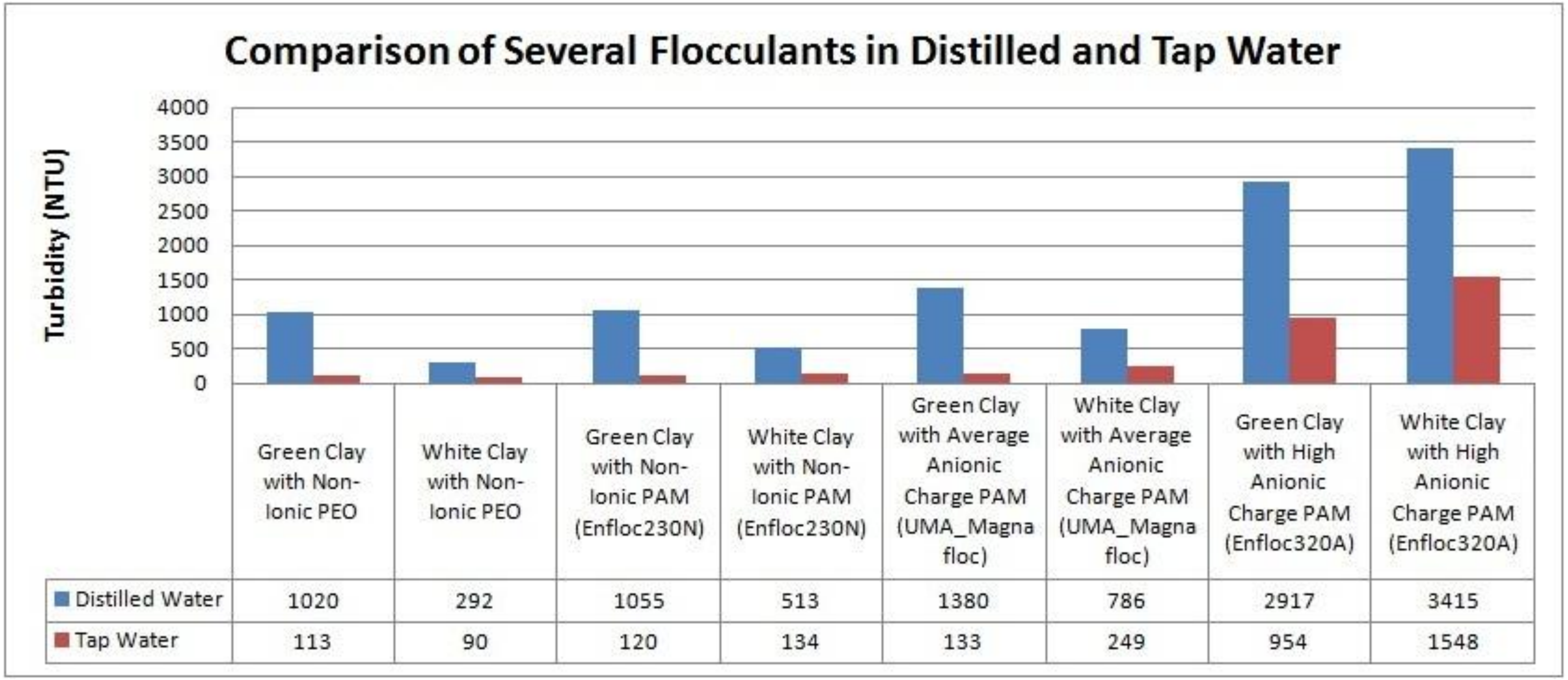
The zeta potentials of the aged clay samples were measured and compared with the fresh samples. The zeta potential of both clay samples became less negative (from -41.20 to -31.80 mV for the green clay and from -33.50 to -24.20 mV for the white clay) in distilled water at the end of the 24 hour aging period. It was obvious that the zeta potentials of the clay surfaces became less negative upon aging of clay samples. The green clay flocculation that resulted in good turbidity removal after aging may be explained by zeta potential. Because less negative zeta potentials may lead to decrease in the repulsion between polymer and particle and it was concluded in good flocculation performance. On the other hand, the same explanation was not valid for the flocculation of the white clay suspension. The flocculation performance of the white clay suspension significantly decreased (Figure 40) upon aging although the zeta potential of the white clay particles became less negative (from -33.50 mV to -24.20 mV).

4.10 Comparison of Several Flocculants in Distilled and Tap Water

Nonionic, average anionic and high anionic charged flocculants were tested in distilled water and tap water and test results were plotted in Figure 41 according to the order of increasing anionic charge. The cationic charged flocculant types were not used because they have lower molecular weight (< 1 million) than anionic and nonionic flocculants (up to 20 million) and also they are very sensitive to high pH; cationic polymers coiled up and behaves opposite of anionic and nonionic flocculants (Figure 38) at high pH values (Skuse, 2002), namely stretch conformation does not occur for an effective flocculation process (Besra et al., 2004). For the purpose of determining the place of new UMA Magnafloc flocculant among other conventional flocculants, the results were plotted in Figure 41 according to increasing anionic charge density of the polymers from left-hand side to right-hand side. It was found that increasing ionic charge of polymers resulted in increasing supernatant turbidity values and poor flocculation. As explained previously, original pH of the pulps were very high (pH 9.40) and that was caused by high negatively charged clay surfaces that may repel anionic polymers. UMA Magnaflocs took places at the middle of the graph between the nonionic and high anionic charged polymers due to its average anionic character.

High anionic charge flocculant (Enfloc320A) yielded exceptionally very high turbidity results. The turbidity results of the high anionic charged polyacrylamide were 2917 NTU (954 NTU in tap water) for the flocculation of the green clay suspension and 3415 NTU (1548 NTU in tap water) for the flocculation of the white clay suspension in distilled water. When other flocculants turbidity results were compared with those values, high anionic charge flocculant cause dramatically high turbidity values even in the tap water. The reason of that was most probably due to very high repulsion forces between negatively charged particles and anionic polymeric macromolecules. This repulsion may decrease the adsorption of polymers on the active surface sites that resulted in poor flocculation performance.

The green clay flocculation’s turbidity values were very high (around 1000 – 1300 NTU) in distilled water (excluding Enfloc320A) whereas the green clay suspensions were much more easily flocculated in tap water down to around 110 – 130 NTU with nonionic polyacrylamide, nonionic polyethylene oxide and average anionic charge polyacrylamide. Similarly, the white clay flocculation experiments were resulted in high turbidity values (around 292 – 786 NTU) in distilled water (excluding Enfloc320A). When tap water and distilled water were compared with each other as a medium, it can be said that the tap water was more favorable with the turbidity values of 90 - 249 NTU. In addition to that it was observed that the turbidity values of the flocculation of the white clay suspensions were always lower than the green clay in distilled water or tap water conditions when the nonionic to medium anionic range flocculants were used.



	Green Clay with Non-Ionic PEO	White Clay with Non-Ionic PEO	Green Clay with Non-Ionic PAM (Enfloc230N)	White Clay with Non-Ionic PAM (Enfloc230N)	Green Clay with Average Anionic Charge PAM (UMA_Magna floc)	White Clay with Average Anionic Charge PAM (UMA_Magna floc)	Green Clay with High Anionic Charge PAM (Enfloc320A)	White Clay with High Anionic Charge PAM (Enfloc320A)
🟦 Distilled Water	1020	292	1055	513	1380	786	2917	3415
🟥 Tap Water	113	90	120	134	133	249	954	1548

Figure 41. Comparison of Several Flocculants in Distilled Water and Tap Water (100ml-Fixed Dosage of Each Polymer; %3 Clay; 3% Borax; pH=9.40)

In all flocculation experiments including several flocculants, significant differences were observed between distilled water and the tap water in terms of the supernatant turbidity values. The properties of the tap water and distilled water were tried to be identified previously (Table 17 and Table 18) by using Lovibond SensoDirect Con200 Conductivity/TDS/Salinity Meter. Whereas total dissolved solid (TDS) in distilled water was 3 mg / L, it was found 552 mg / L in tap water. In addition to that, the distilled water was normally classified as “very soft” in terms of French water hardness scale (this scale is currently used in Turkey water standard, (Boysan and Şengörür, 2009)) although the tap water was classified as “very hard”. The advantageous effect of the tap water may be explained with very high TDS (according to US National Secondary Drinking Water Regulations, maximum value of TDS in tap water can be 500 mg / L (Wallace, 2008)) and its hardness (Table 17 and Table 18).

In conclusion, nonionic polymers may be more suitable for the flocculation of Kırka tincal clays. Especially, polyethylene oxide type polymeric flocculants seems to be more effective on both clay samples. It can be explained that nonionic flocculants are less sensitive to pH variations, ions type, surface charge of particles and solid amount of suspension or solution (Lu et al., 2005).

4.11 Infrared Studies

FTIR analysis reveals important information about minerals; their active surface sites, surface reactions including bonding mechanisms, surface modification, adsorption behavior and flotation and chemical dewatering reagents effect on mineral (Riviere & Myhra, 2009). Moreover, ATR (attenuated total reflectance) mode of FTIR spectroscopy was recommended especially for clay samples and their chemical processes in aquatic solutions and polymer adsorptions (Sposito, 2004, p. 55). El-Midany (2004) stated that the leading researchers like Paradip & Moudgil (1991); Behl and Moudgil (1993); Kyselev and Rygin (1972); Zaman (2002); Mathur and Moudgil (1997) preferred this method related to the concept for the purpose of polymer – solid interaction analysis. In this study, similar path will be followed and the clay surfaces will be tried to explain with ATR-FTIR in the scope of flocculation.

4.11.1 ATR FT-IR Analysis on the Green Clay Sample

Infrared analysis result of the green clay sample was potted in Figure 42. The bands at 1437 cm^{-1} indicates to the carbonate mineral presence (Gunesekaran & Anbalagan, 2007). The other bands at 729, 877 cm^{-1} proves that it's a natural dolomite. Silicate presence was also proved with Al and Si deformations and bendings. Their wavenumbers 978, 644 and 530 cm^{-1} may be considered that montmorillonite. Also, there was a shoulder at around 978 cm^{-1} and this shoulder was due to Si – O stretching of layered silicate (Moudgil & Behl, 1993) .

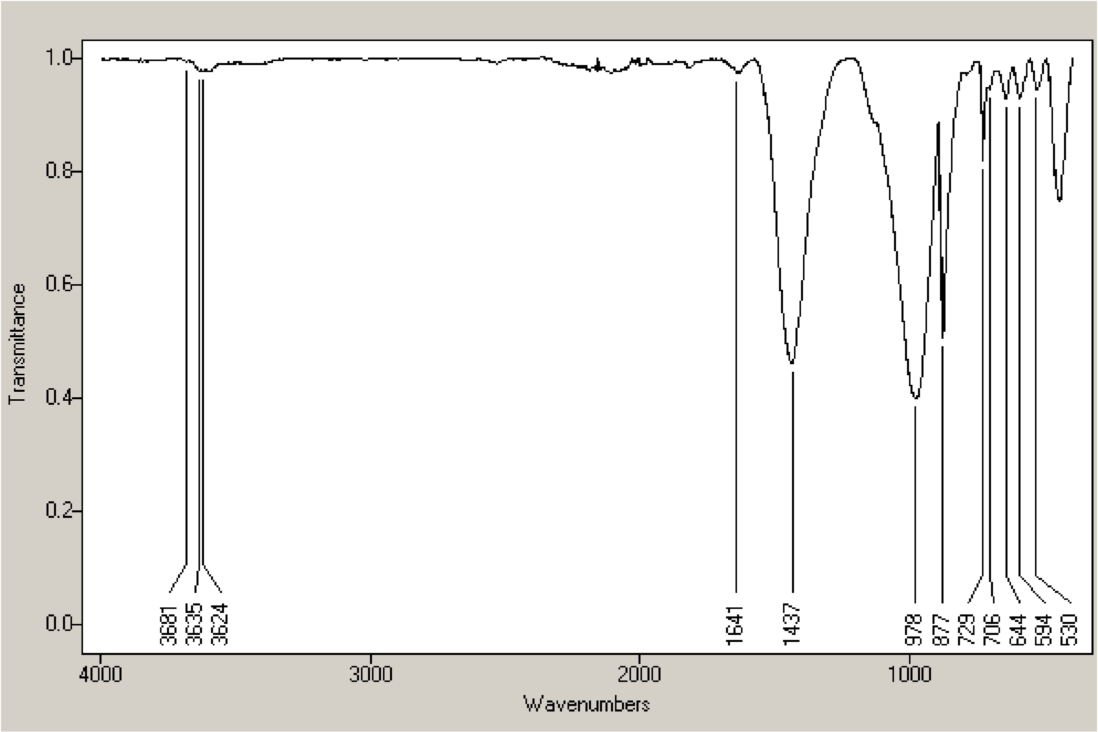


Figure 42. ATR-FTIR Analysis of Green Clay

Infrared analysis was carried out for the Ca treated and Mg treated green clay suspensions for the purpose of identification of surface modification. The results were shown in Figure 43 that there was an important increase in the 1645 cm $^{-1}$ peak. The black line was the original sample; the blue line was Mg – treated clay and red line represents Ca – treated. This increase in the peak 1645 cm^{-1} indicated the increase of H – O – H bending band of water that means adsorbed water layer increase on the surface of clay (Donstova et al., 2004).

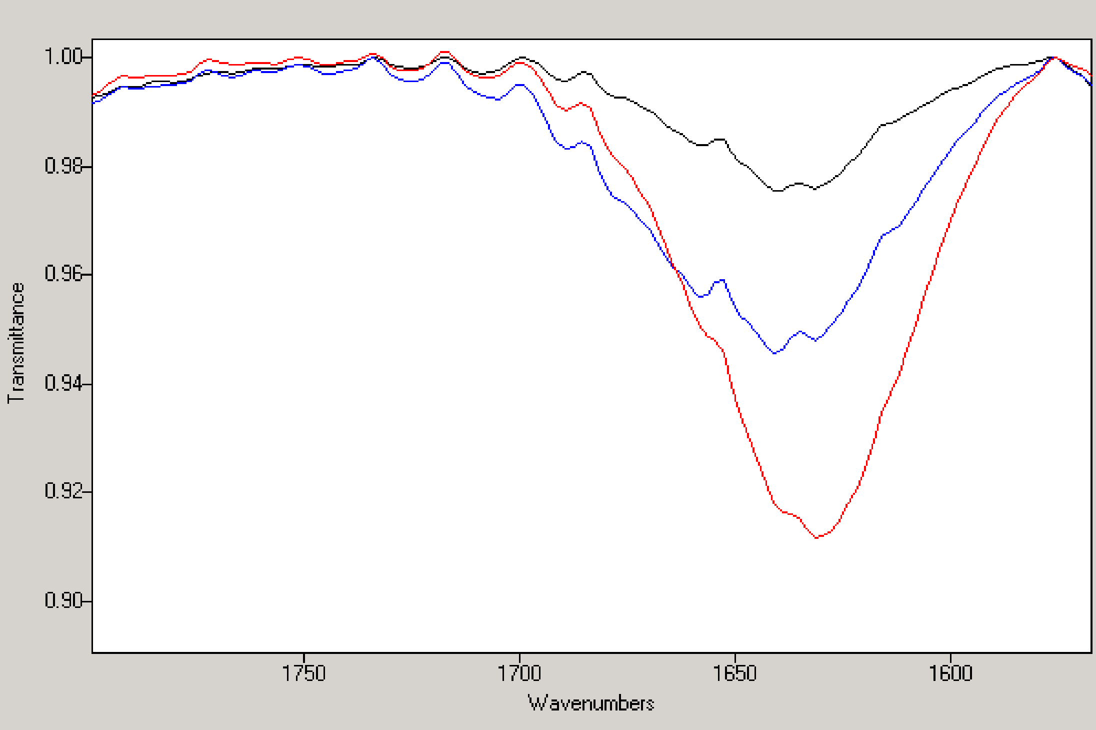


Figure 43. Adsorbed Water on the Surface of Green Clay: a) Black Line: Original Sample b) Blue Line: Magnesium Treated Sample c) Red Line: Calcium Treated Sample

This increase was explained by Langmuir (1997). He stated that water molecules had locally unsatisfied negative and positive charges (Figure 44) which associated with the oxygen atom and hydrogen atom in the molecule due to their naturally unique dipolar structure. This dipolar charge distribution resulted in contact between water molecules and cations. Because, water molecules oriented with their oxygens toward the cation (Calcium and magnesium in the scope of this thesis) and their protons away from it as shown in Figure 44. Furthermore, the right hand side of Figure 44 schematically explains a cation aqua-complex with the water molecules oriented around the cation in naturally six- or four- fold coordination (Langmuir, 1997, p. 85). This explanation revealed the reason of increase in the infrared peak because adsorbed calcium and magnesium in aqua-complex form increased the water amount on the surface.

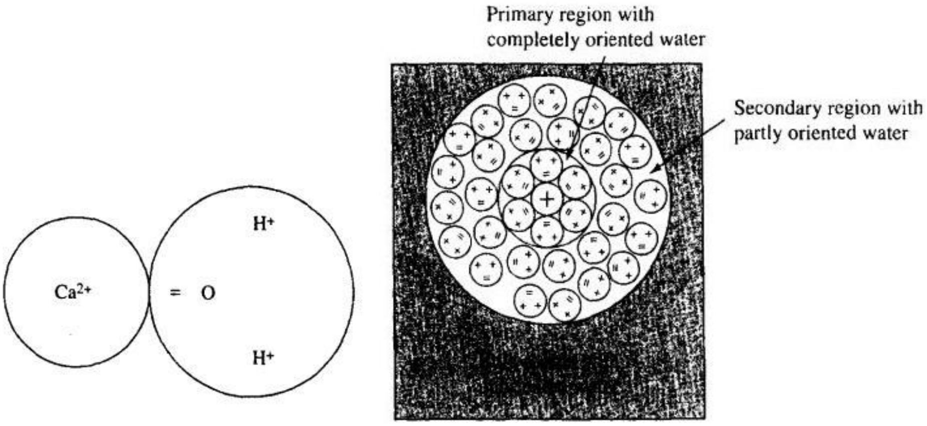


Figure 44. Aqua – Complex of Calcium (Langmuir, 1997)

Also, an important increase was observed between 3100 and 3680 cm^{-1} (Figure 45). This increase was also due to adsorbed water and Donstova (1999) indicated that this region represents the secondary H – O – H bending and free O – H stretching (Figure 46). To identify and differentiate them was not easy because they were overlapped and O – H stretching seemed to be a shoulder of the secondary water bend peak. In spite of that, it may be claimed that free O – H amount on the clay surface increased especially in calcium availability.

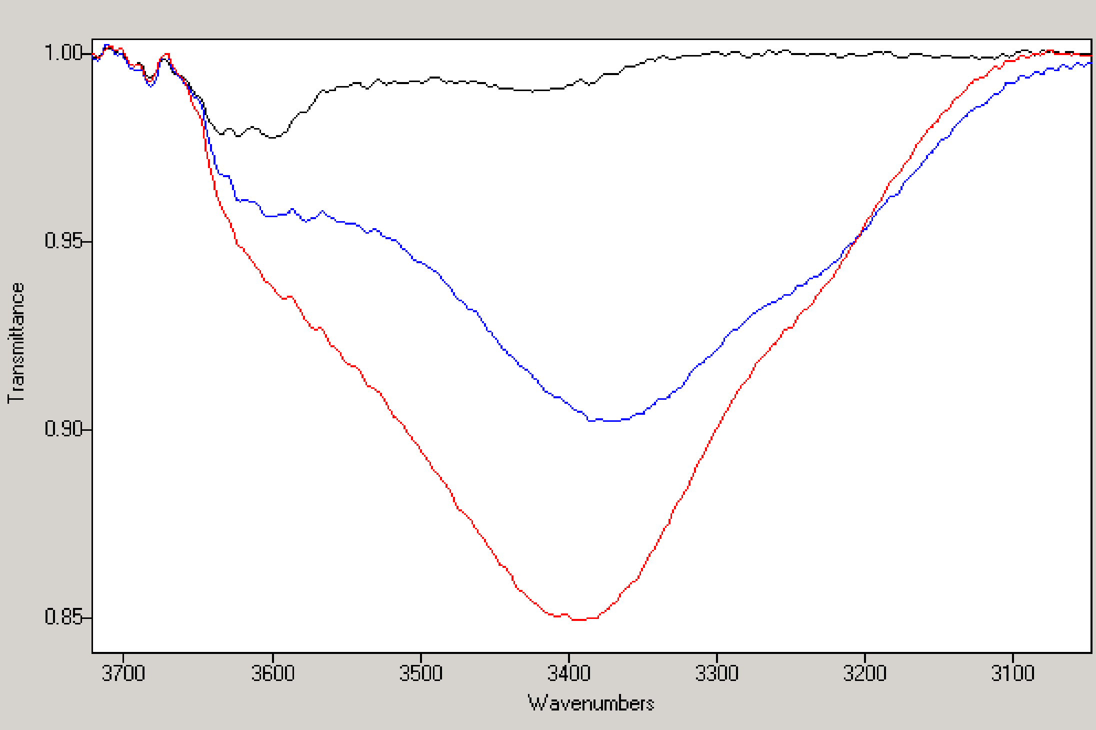


Figure 45. Free OH Region of Green Clay: a) Black Line: Original Sample b) Blue Line: Magnesium Treated Sample c) Red Line: Calcium Treated Sample

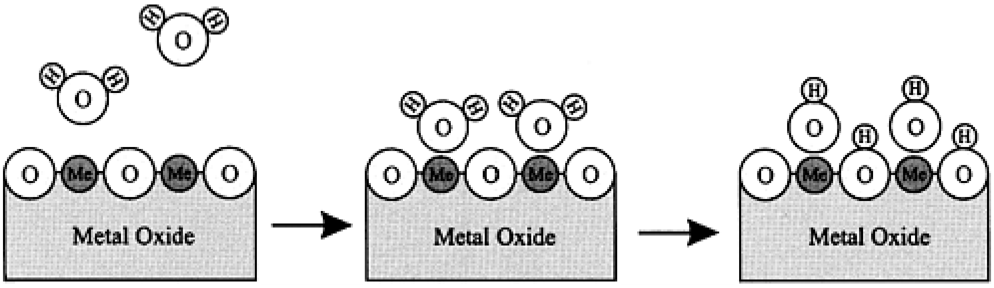


Figure 46. Mineral Surface Interaction with Water and Formation of Isolated OH Groups

Somasundaran (2004) also stated that there was dependence between H – O – H bending and O – H stretching. The surface of a mineral in contact with water was hydrated at first. Water molecules adsorbed on the surface and only then, it is hydroxylated (Figure 46). Hydroxylation phenomenon is explained that hydrogen start to move from the adsorbed molecule of water to the oxygen atom of the oxide on mineral surface. In conclusion the active sites free OH groups forms as showed in Figure 46 but the "adsorption" is prerequisite for the "hydroxylation" (Somasundaran and Hubbard, 2004).

In conclusion, O – H stretching formation and its increase in the infrared results are very important in terms of the flocculation process because the free O – H groups on the surface has the ability to bond flocculants. The reason of significant improvement in flocculation with calcium availability may be explained with these inferences.

The Infrared measurement was also carried out individually for the green clay and polymer treated (flocculated clay) green clay sample to prove adsorption sites. Figure 47 belonged to the green clay. As it was observed the peaks intensities were very weak. But, 3599, 3608, 3620, 3627 and 3628 cm^{-1} peaks were identified as possible free OH groups.

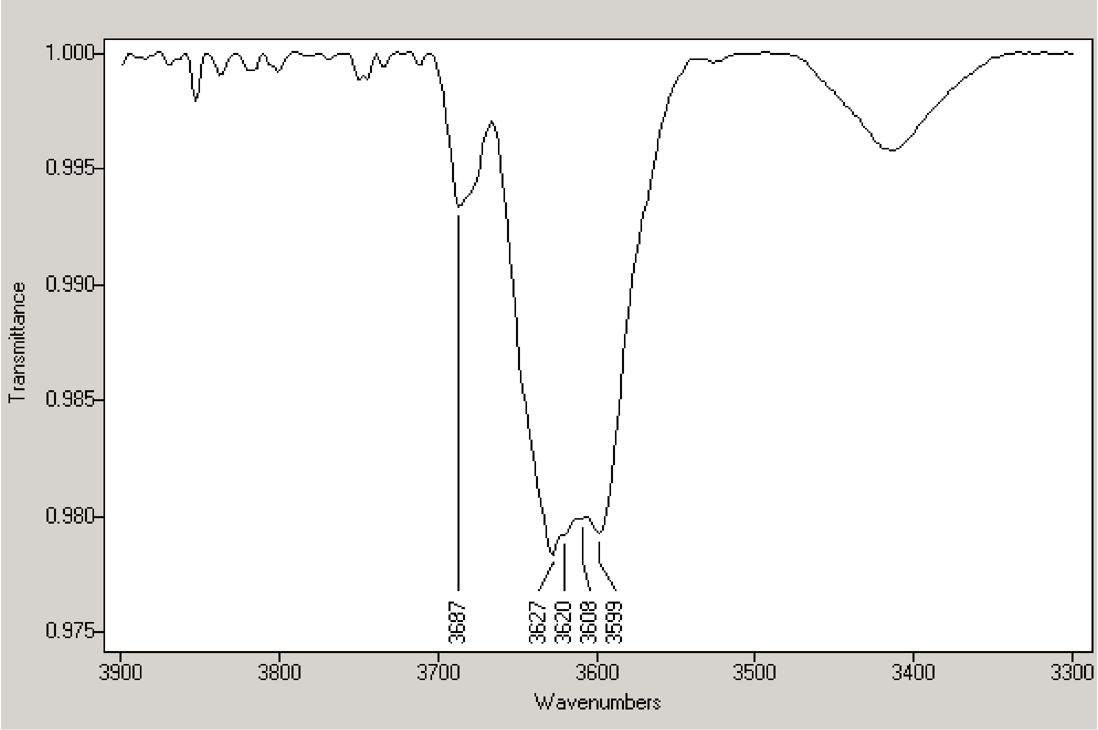


Figure 47. Detailed Infrared Spectrum of Isolated OH Region of Green Clay before Polymer Adsorption

When polymer + clay infrared result in Figure 48 was compared to Figure 47, it was observed that the peaks: 3608 and 3620 cm^{-1} vanished and also the intensity of other peaks especially at 3627 cm^{-1} decreased. This observation can be concluded that the adsorption of polymer on the green clay particles occurs through isolated –OH groups (act like a specific chemical groups) and hydrogen bonding mechanism was formed between polymer and clay surface.

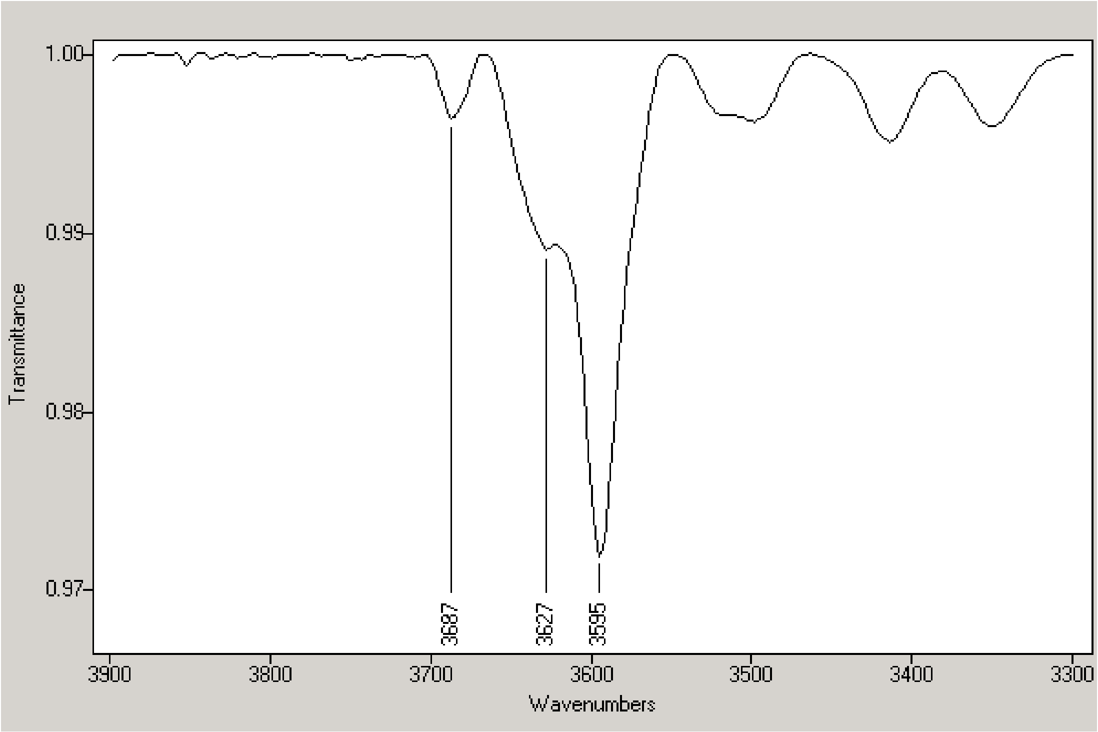


Figure 48. Detailed Infrared Spectrum of Isolated OH Region of Green Clay after Polymer Adsorption

4.11.2 ATR FT-IR Studies on White Clay Sample

Similar infrared result was obtained for the white clay when compared to the green clay (Figure 49). The bands at 1425, 729, 876 cm^{-1} indicates to dolomite mineral presence (Gunesekaran and Anbalagan, 2007). Al and Si deformations and bendings were also detected in the results. Their wavenumbers 984, 652 and 530 cm^{-1} may be considered as montmorillonite (mixed layer with illite). Moreover, the shoulder near the 984 cm^{-1} may be named as Si – O stretching (Davarcıoğlu & Çiftçi, 2009).

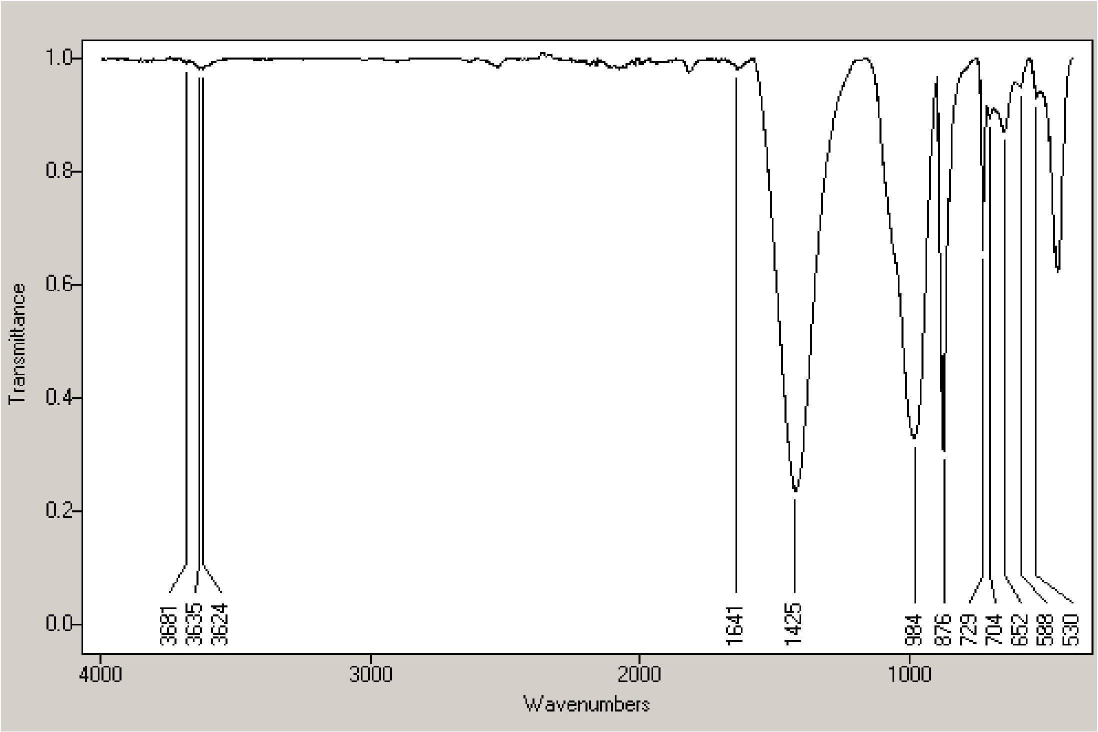


Figure 49. ATR-FTIR Analysis of White Clay

Ca and Mg adsorption caused the surface modification of the white clay similarly to the green clay (Figure 50). The peak intensity at 1645 cm^{-1} indicated to the adsorbed water on the clay. It may be concluded that (black line original sample, blue line magnesium treated and red line calcium treated sample) Ca – treated sample adsorbed more water than magnesium treated water and original sample on the surface.

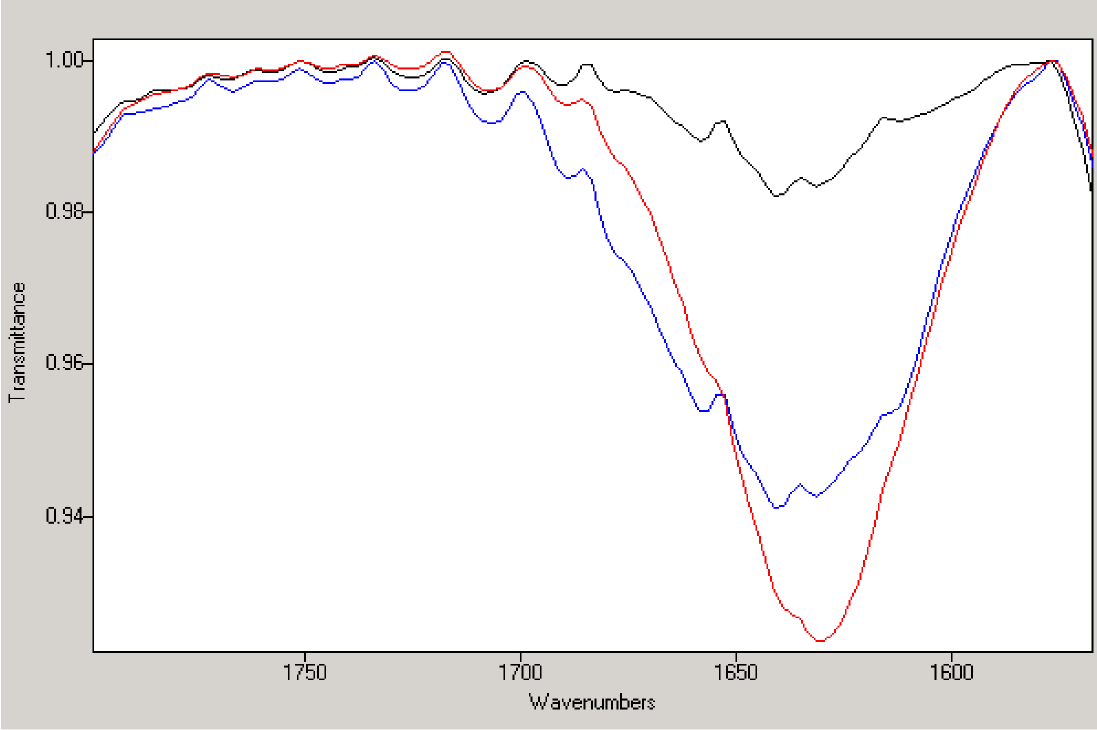


Figure 50. Adsorbed Water on the Surface of White Clay: a) Black Line: Original Sample b) Blue Line: Magnesium Treated Sample c) Red Line: Calcium Treated Sample

Another measurement was carried out in the rage of 3100 and 3680 cm^{-1} (Figure 51). This region represents the overlapped peaks that represent secondary H – O – H bendings and isolated O – H stretching according to Donstova (1999). Although clear identification was challenging due to overlapping, the increased in the 3600-3680 cm^{-1} was obvious that indicated to the free OH groups that named specific active chemical groups that can establish hydrogen bonding mechanism between clay surface and polymer.

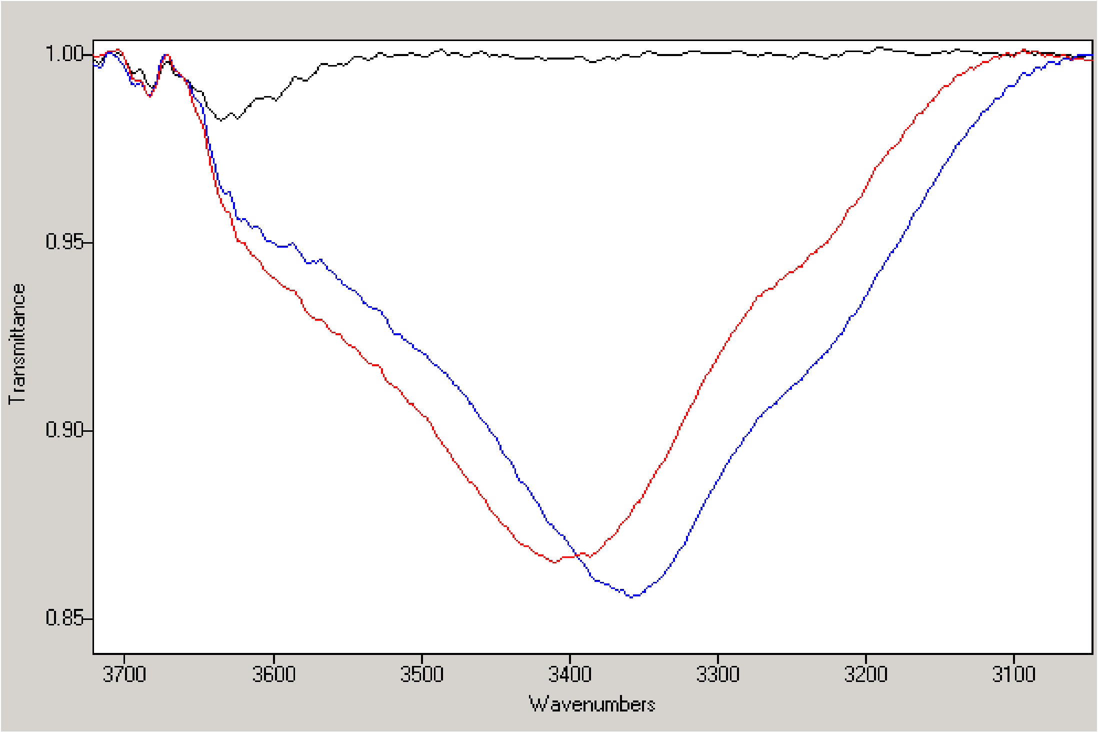


Figure 51. Free OH Region of White Clay: a) Black Line: Original Sample b) Blue Line: Magnesium Treated Sample c) Red Line: Calcium Treated Sample

The white clay and polymer treated (flocculated) clay was also individually measured with FTIR to differentiate the difference for the purpose of identify where the bonding takes place. The only peaks identified were at 3629 and 3681 cm^{-1} as showed in Figure 52.

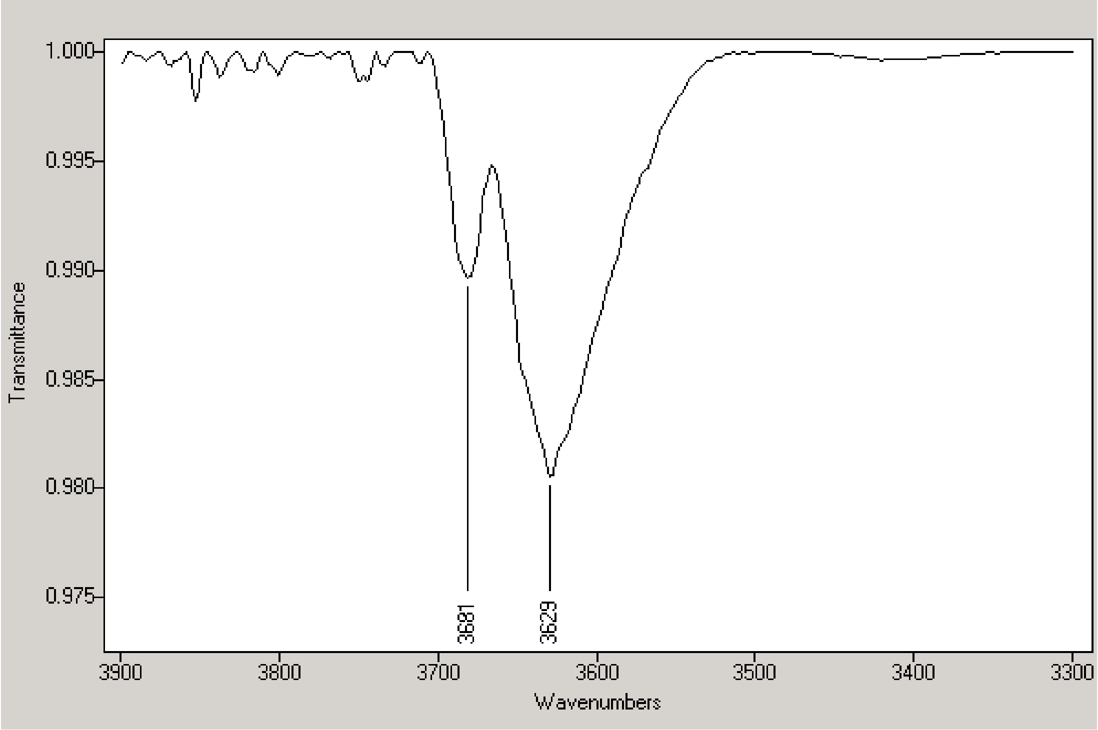


Figure 52. Detailed Infrared Spectrum of Isolated OH Region of White Clay before Polymer Adsorption

The peaks at 3620 and 3608 cm^{-1} that took place in the green clay flocculation and identified as active chemical sites for the polymer adsorption could not be observed for the white clay. Furthermore, there was no disappearance detected in the FTIR plots of polymer added white clay (Figure 53) and individual white clay (Figure 52). In spite of that, small change in the wavelength position was observed and just small amount of decrease occurred in their intensities of 3683 and 3627 cm^{-1}. In conclusion, although flocculation substantiated with naked eye, no difference in the spectra was observed with and without polymer. Moudgil and Behl (1993) carried out some infrared studies with polymeric flocculant and dolomite sample for the purpose of explanation the mechanism of dolomite flocculation similar to the scope of this thesis but they could not succeed in substantiating the adsorption mechanism.

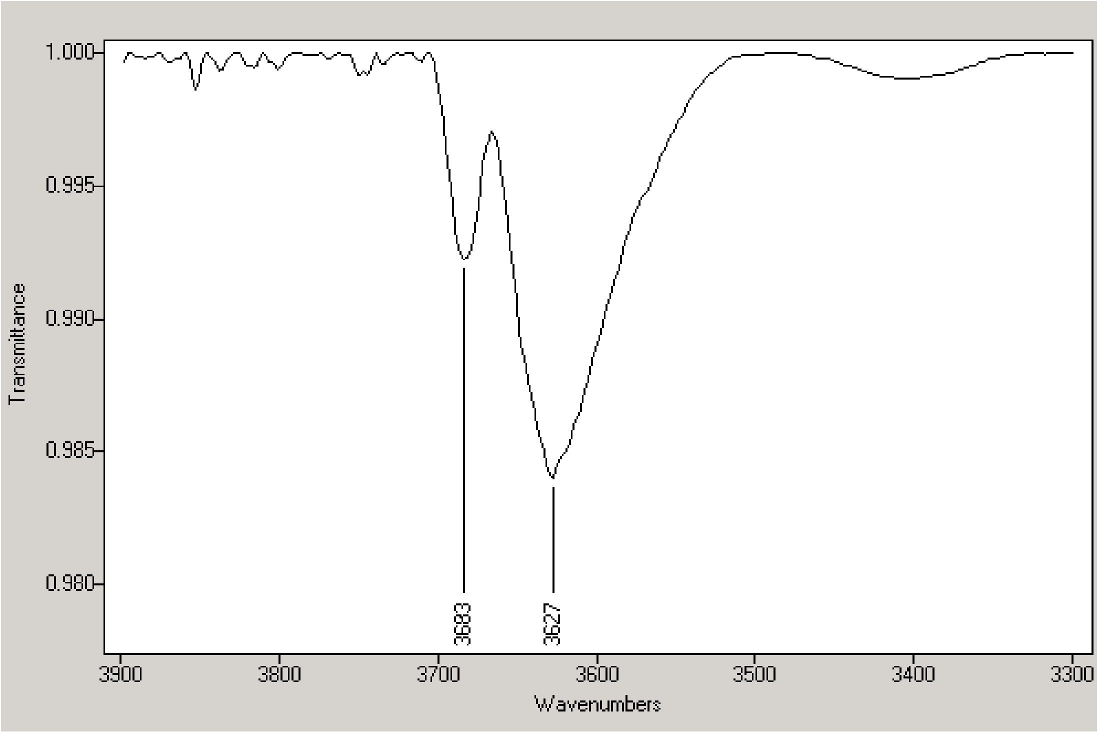


Figure 53. Detailed Infrared Spectrum of Isolated OH Region of White Clay after Polymer Adsorption

CHAPTER 5

CONCLUSION

Based on the results and discussions presented in the scope of this thesis, the following outcomes can be derived:

1. Flocculation behavior of the green and the white clay suspensions is different from each other at pH 9.40 (alkaline pH due to borax buffering capacity) and the flocculation of the green clay suspension results in greater turbidity than the white clay suspension in distilled water. The turbidity removal of the clay suspensions with single-stage flocculation seems also impossible and the additional polymer treatment is required to completely remove the turbidity. However, this two-stage flocculation process leads to a substantial amount of polymer consumption.

2. The flocculation performance of these problematic clay suspensions can be enhanced by adding a proper cation like Ca into the system or adjusting pH of the suspension from 9.40 to 7.00. Especially at neutral pH, the flocculation behavior of the green and white clay suspensions resembles each other due to increased performance of the polymer. Nevertheless, the pH adjustment is not easy because the presence of borax buffers the solution and leads to very high acid consumption.

3. Aging is also changing the flocculation behavior of the green and white clay suspension. The flocculation of the white clay suspension become much poorer as compared to the green clay suspension after the aging period.

4. The flocculation experiments including several flocculants prove that non-ionic polyacrylamides and polyethylene oxides are more effective than the high anionic charged polymers at alkaline pH 9.40.

5. ATR-FTIR analysis proves that presence of the cations in the suspensions leads to increasing amount of adsorbed water and surface-active groups on the surface of the clay samples. Furthermore, ATR-FTIR results verify that the polymers attached themselves on the surface of the clay samples through hydrogen bonding mechanism.

Based on the experience gained during this thesis, the followings can be recommended for future extension of the work:

1. Alternative flocculant aids can also be experimented for the purpose of improving flocculation.

2. Further alternative water treatment techniques can be studied to decrease very high polymer consumption for the flocculation of the Kırka clays.

3. Mechanical dewatering equipments can also be tested with the combination of flocculant and coagulant.

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