

NOVEL SEPARATION METHODS FOR REMOVING NANOPARTICLES AND COPPER FROM CHEMICAL MECHANICAL PLANARIZATION WASTES

by

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ABSTRACT

Chemical mechanical planarization (CMP) wastewater emanating from semiconductor processing contains copper (II) ions and either alumina and/or silica nanoparticles. The efficiency of biotreatment schemes to remove copper before water recycling or disposal is improved when the nanoparticles are removed before biotreatment. Therefore, coagulation of nanoparticles and filtration were studied in order to identify the most viable and optimal way to employ coagulants using common methodologies for wastewater treatment.

It is difficult to separate nanoparticles from CMP wastes through settling and conventional filtration. Chemical aggregation of nanoparticles was found to enhance the settling and filtration characteristics. The efficiency of five chemical coagulants was evaluated, and reagents were based on aluminum and iron salts, natural coagulant and polyelectrolytes with different electrical charge. Optimal operating conditions such as coagulant dosage, pH, type of coagulant, and sedimentation time were established. These parametric studies demonstrated the viability of coagulants to reduce the amount of particles in wastes. Over 95% turbidity reduction was achieved and less than 5 NTU (the recommended value for good quality water) was realized. Filtration characteristics of aggregated particles were also established. To realize the goal of water recycling, it was imperative to develop a rapid and efficient technology taking into account the characteristics and complexity of this waste as well as the interactions between coagulants and nanoparticles.

RESUMEN

Los efluentes provenientes del proceso de planarización químico-mecánica (CMP, por sus siglas en inglés) contienen tanto iones de cobre (II) como nanopartículas de alumina y/o silica. La eficiencia de los esquemas de biotratamiento para remover cobre antes del reciclaje o desecho del agua es mejorado cuando las nanopartículas son removidas antes de este tratamiento. Por lo tanto, la coagulación de nanopartículas y filtración fueron estudiadas con el fin de identificar la manera más viable y óptima de emplear los coagulantes comúnmente utilizados para el tratamiento de agua y efluentes.

Es difícil separar las nanopartículas de los efluentes del CMP mediante sedimentación y filtración convencional. La agregación química de nanopartículas mejoró la sedimentación y las características de filtración. La eficiencia de cinco coagulantes químicos fueron evaluados y estos son sales de aluminio y hierro, un coagulante natural y polielectrolitos con diferente carga eléctrica. Se establecieron las condiciones óptimas de operación tales como dosificación de coagulante, pH, tipo de coagulante y tiempo de sedimentación. Estos estudios paramétricos demostraron la viabilidad de los coagulantes para reducir la cantidad de partículas en los efluentes. Se obtuvo una remoción de turbidez superior a 95% y menos de 5 NTU, lo cual es recomendable para un agua de buena calidad. Las características de filtración de las partículas agregadas también fueron establecidas. Para lograr el propósito de reciclar agua, fue imprescindible desarrollar una tecnología rápida y eficiente tomando en consideración las características y complejidad de este efluente así como las interacciones entre los coagulantes y nanopartículas.

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CHAPTER 1: INTRODUCTION

In the past hundred years, technology has drastically improved the quality of human life in most parts of the world. However, it has also increased demand on natural resources as well as multiplied the amount of waste that is produced; especially on our water resources which are being seriously contaminated.

Nowadays, throughout the world there is a serious concern because of an overall shortage of clean water resulting from the effects of climate change as well as the rapid increase in world population. However, the need for water conservation is one of the most pressing global issues today.

Electronic industry is one of the most fast growing sectors of economy in many countries around the world for the past several decades, and that has greatly impacted the way in which we live. Semiconductor is one of the key components of the electronic and electrical products. Their impact is seen in our current days and is present in computers and their peripherals, communication equipment, consumer electronic products, electronic control devices, and scientific and medical test equipment.

Manufacturing of semiconductors involves numerous, highly complex processes. Chemical mechanical planarization (CMP) represents a relevant step used to diminish semiconductor wafer surface imperfections by means of chemical and mechanical forces.

The semiconductor manufacturing involves over 200 of high purity organic and inorganic compounds in which a large amount of ultrapure water is consumed in various washing and cleaning steps. Typically, a 200 mm wafer fab processing 40,000 wafers per month uses

between 2 and 3 million gallons of water per day where CMP effluents can account for 30-40% of the water discharge (Golden *et al.*, 2000). For this reason it is important to establish a strategy to reduce water consumption, explore the possibility of recycling water in non-process applications such as in cooling towers and scrubbers, and comply with environmental regulations (U.S EPA) in order to completely degrade pollutants and lead to environmentally benign compounds as end products. Thus, organic and inorganic contaminants should completely be removed from effluents.

The present work has been developed at the Department of Chemical Engineering of the University of Puerto Rico in conjunction with its counterpart at the University of Arizona. The objective of this project was to develop a high-efficiency and novel method to separate nano-sized alumina-silicate particulates and copper from CMP wastewater. This entailed the following tasks:

- (i) Characterizing and testing CMP wastewater;
- (ii) Conducting chemical coagulation tests and filtration to remove nano-size alumina and silica particulates and copper, mainly present in this wastewater.

Its purpose was to establish a novel separation method for removing nanoparticles and copper from CMP waste. Inorganic, organic (polyelectrolyte) and natural coagulants were used to carry out this goal.

1.1. Justification

Treated and untreated industrial effluents and other injectable or semi-solid wastes, which are potential pollutant streams, are disposed of in water bodies (rivers, lakes, bays or oceans), landfills, caves, and in depleted wells or aquifers. At the same time, rivers, lakes and aquifers are the main sources of groundwater a vital resource for healthy living. The cumulative effect of industrial effluents can lead in many ways to interaction with the vital water resources leading to contamination. This must be prevented through a concerted effort by academia, industry and regulatory agencies.

There are several examples where the cumulative effect of releasing treated water has led to serious issues. A fuel additive such as methyl tert butyl ether (MTBE) and perchlorate from surrounding industries have been identified as serious contaminants in water resources of the western states of the USA (Richardson, 2003). In general wastewater generated in food, biotechnology, microelectronics and biotechnology/ pharmaceutical industries often contains dispersed multiphases and species that make it difficult and unpredictable to treat. The difficulty is due to both interfacial and multicomponent interactions in separation equipment. The dispersed phases could be oils and/or grease from tuna plants (Melendez, 2002), tars in wastewater from racemic mixtures, nanoparticle-abrasives in microelectronics industries (Golden *et al.*, 2000; Stanley & Ogden, 2003), and suspended organics or other components which tend to assume particulate forms as found in municipal, food or pharmaceutical industry.

1.2. Objectives

Chemical mechanical planarization (CMP) wastes will be treated by employing methods based on novel separation techniques. The main objective of the study is to establish effective coagulants and operating parameters for efficient removal of nanoparticles and its removal before biotreatment of CMP wastes. The study will establish the right coagulants and optimal parameters for the coagulation process; and its eventual effect on the efficiency of biosorption of copper during biotreatment.

The overall objective is to reduce water consumption in this process and explore the possibility of recycling this vital resource. In the same way, it is imperative to comply with environmental regulations (U.S. EPA) and reduce cumulative effect of pollutant effluents that would adversely impact our environment.

The specific objectives are to:

- (1) Characterize CMP wastes both raw and surrogate ones. Multiphase-multicomponent interactions will be investigated and then this study will establish the effect of nanoparticles on biosorption of copper.
- (2) Study the coagulation process and conduct parametric studies to establish the optimal parameters.
- (3) Develop efficient pathways for removing both nanoparticles and copper from CMP wastes before disposal or reuse. This also focuses on studies of filtration characteristics of coagulated nanoparticles in standardized filters.

The results of the present study may lead to a rapid, efficient, and economical method of treatment of Cu-CMP wastes and water reuse.

CHAPTER 2: PREVIOUS WORK AND LITERATURE REVIEW

2.1 Research efforts towards Environmentally Benign Processing

Environmentally benign processing demands that used water and slurry such as chemical mechanical planarization (CMP) wastes be treated and recycled if possible. CMP wastes contain nanoparticle abrasives such as alumino-silicates, copper and many other compounds (Golden *et al.*, 2000). There is a concerted effort to treat CMP wastes via biosorption (Stanley & Ogden, 2003) and other novel filtration/biotreatment schemes (Padilla, 2006). Stanley and Ogden established that efficiency of biotreatment/biosorption is significantly reduced due to fouling of biosorption bed by the nanoparticles. Thus, the motivation for this study is to develop novel separation processes for removing alumino-silicate nanoparticles from CMP wastes and to establish whether removal of nanoparticles can improve the efficiency of the biosorption step.

Water reuse and treatment is at the heart of environmentally benign manufacturing, since a lot of water is used in the food (Melendez, 2002), pharmaceutical, and semi-conductor industries (Golden *et al.*, 2000). There is a need to recycle water in these industries once the right technologies for treatment are in place. It is proposed in this investigation to develop chemical treatments, filtration and biotreatment schemes for treatment of copper chemical-mechanical-planarization (Cu-CMP) wastewater and CMP slurry and, to eventually be able to recycle water. CMP wastes will be treated via novel separation processes: to remove nanoparticles (aluminum silicate) used as abrasives in CMP processes and to remove Cu. The long-range goal is to develop optimized schemes for water recycle in the biotechnology

and semi-conductor industries. This work will attempt to provide an understanding of the complexity of handling and treatment of dispersed multiphase-multicomponent mixtures. Particularly, this work should provide insights into interactions among species and nanoparticles and how they affect the performance of treatment schemes.

2.2. Background on water treatment and recycle

The growth in urban centers and improvement in quality of life, and manufacturing activities have led to increased consumption of water. Currently, most of the used water in urban centers ends up at wastewater treatment facilities from where it is disposed of into bays or large water bodies (rivers, lakes, seas or oceans). In order to improve the quality of life and water resources, regulatory agencies have imposed high quality wastewater disposal standards. In some parts of the developed world, used water from secondary treatment facilities is recycled for human consumption and other uses including groundwater recharge and irrigation. At industrial scale, however, only part of water (boiler feed water, cooling tower water, and chilled water) is recycled. Water reuse and recycling should be part and parcel of an efficient water resources management scheme. Water resources management schemes should certainly include the large volumes of industrial wastewaters that mostly end up at disposal sites.

To realize the goal of recycling used water, it is imperative to develop a rapid and efficient technology to treat secondary wastewater-treatment effluents. A combination of rapid mass exchangers (low-efficiency filtration, molecular filtration, high-efficiency molecular filtration, followed by or combined with biotreatment) followed by disinfection by

irradiating the treated water with UV light can be optimized to treat secondary wastewater effluents to produce recycled water for human consumption, industrial use, irrigation, and/or artificial recharge. The performance of mass exchangers should be optimized in terms of particulate-separation efficiency, microbial presence detection due to bio-fouling and efficiency in reducing biological oxygen demand (BOD) and certainly, efficiency at removing metals. Treated water can then be analyzed to detect BOD and microbial populations and these data should be compared to natural groundwater. This investigation will attack the problem of treating Chemical Mechanical Planarization (CMP) waste streams containing a mixture of organics, copper, and silica or alumina nanoparticles. These particles are difficult to remove and their presence limits the performance of many treatment schemes. CMP is a critical step in integrated circuit (IC) device manufacturing (Stanley & Ogden, 2003) in which CMP and post-CMP cleaning processes account for 30-40% of the water consumed by IC manufacturers and produce large quantities of wastewater (Golden *et al.*, 2000).

2.3. CMP slurries and wastewater

Chemical Mechanical Planarization (CMP) is the process of planing and smoothing the wafer surface by chemical and mechanical forces. CMP slurries are needed in microelectronics industry because wafer polishing depends on them to clean its surface and remove imperfections. Due to rapid growth, the semiconductor industry consumes large volumes of ultra pure water in CMP slurries and post-polishing cleaning (Golden *et al.*, 2000). CMP slurries once used in the polishing processes pick up inorganic ions such as

copper which is a known carcinogen (World Health Organization, 1998) and toxic to flora and fauna in aquatic systems. Therefore, it is a requirement to treat CMP wastes in order to remove copper. This work will focus on studies of Cu-CMP waste, since according to regulations the amount of copper in the effluent treated water should be less than 0.1 to 3.0 ppm (Reker *et al.*). In order to develop effective methods of treatment of CMP wastes, it is imperative, first and foremost, to study its characteristics or complexity.

2.3.1. Characteristics of CMP slurries and wastewater

CMP wastewater is very complex and its chemistry is difficult to characterize because of the proprietary nature of CMP slurries and processes. The wastes are different for each CMP process and depend upon tool type, drain segregations, slurry chemistry and CMP process type (Reker *et al.*). As reported by Golden *et al.* (Table 2.1), CMP wastewater in general is known to include *inorganic ions and oxides* (including copper), *suspended and settled abrasive particles* (silica, alumina, manganese, cesium), *oxidizers, strong acids and weak acids, strong bases*, and *organic materials* (dispersants/surfactants, corrosion inhibitors, metal complexing agents, and organic acids). Since polishing slurries consist of 5 to 10 percent of very fine particles, surfactants are added to slurries to maintain good stability of the suspended solids in the slurry. Subsequently, CMP wastes of varying compositions have been used in a number of treatment studies. The slurries are characterized according to: pH, conductivity, turbidity (indicative of particle content), particle size distribution, metal ion content, suspended solids, dissolved solids, and chemical oxygen demand.

Table 2.1. Materials in CMP wastewater

Inorganic Materials	
Interconnect:	Cu^{2+} , complexed Cu^{2+} , Cu_2O , CuO , $\text{Cu}(\text{OH})_2$, WO_3 , Al_2O_3 , $\text{Al}(\text{OH})_3$, $\text{Fe}^{2+}/\text{Fe}^{3+}$
Barrier/liner:	Tantalum and titanium oxides and oxynitrides
Abrasives:	SiO_2 , Al_2O_3 , MnO_2 , CeO_2
Oxidizers:	hydroxylamine, KMnO_4 , KIO_4 , H_2O_2 , NO_3^-
Strong acids and weak buffering acids:	HF , HNO_3 , H_3BO_3 , NH_4^+ , citric acid
Strong bases:	NH_3 , OH^-
Organic Materials	
Dispersants/surfactants:	poly(acrylic acid), quaternary ammonium salts, alkyl sulfates, EDTA
Corrosion inhibitors:	benzotriazole, alkyl amines
Metal complexing agents:	EDTA, ethanol amines, oxalic and citric acid
Acids:	poly(acrylic), oxalic, citric, acetic, peroxy acetic

2.3.2. Treatment studies of Cu-CMP wastes

A concerted effort is underway to treat CMP wastes. Reker and co-workers demonstrated that crossflow filtration and ion exchange can be used to treat and recycle water from Cu-CMP wastewater. Their studies focused on microfiltration, ion-exchange (for copper removal) and electrowinning. The crossflow filtration was based on polyester fabric media microfilter and it was evaluated for effective removal of suspended particles and for effluent flux across the filter. The studies however did not report the particle size

limit that can be retained by the membrane. However, another study by Lee and co-workers (Lee *et al.*, www.MyKrolis.com), demonstrated through point-of-use filtration lifetime for CMP slurries that filtration of 1.0 μm particles is possible using 0.5 μm filters. Furthermore, these studies established filter life for point-of-use CMP slurry filtration to remove large particles. Preliminary studies have shown that raw CMP slurries sold on the market are highly concentrated especially with particles, and under certain conditions, yet to be established, the particles tend to agglomerate. Raw slurries are diluted before use; however, nonuniformity in particle size leads to defects on the wafer and that is why point-of-use filtration is necessary. In the study of Reker *et al.*, it was identified that the key factors for the success of ion-exchange step are: removal of total suspended solids to prevent resin fouling, reduction of copper, and removal of oxidizers which can oxidize and destroy ion-exchange resin. The major performance parameters sought by Reker *et al.* were: Cu analysis (of raw and filtered water samples and sample after ion-exchange); total suspended solids; and total dissolved solids.

The study illustrated that a two-step process is needed to remove both copper and nanoparticles revealing the limitations of conventional separators due to multiphase-multicomponent interactions. Another recent study (Yang & Yang, 2004) focused on reclaiming high quality water from treating CMP wastewater by a novel crossflow electrofiltration/electrodialysis process. Yet, another study also demonstrated that a two step process (Lin & Yang, 2004) combining chemical coagulation and reverse osmosis was effective at treating CMP wastewater.

Many recent studies have focused on treating CMP wastewater to remove copper and silica nanoparticles via electrocoagulation (Lai & Lin, 2003, 2004; Lin & Yang, 2004; and Den & Huang, 2005). Other studies (Lazaridis *et al.*, 2004; Valenzuela *et al.*, 2005) focused on removing copper from mine and mineral wastewater. In the reported studies that dealt with treatment of CMP wastewater, it was demonstrated by Lai & Lin (2003) that electrocoagulation with aluminum/iron pair achieved 99 % copper removal, over 96 % turbidity reduction, 75 % chemical oxygen demand (COD) reduction or less than 100 mg/L COD in the effluent. The CMP waste slurries studied contained high total suspended solids with particles 68 to 120 nm, high turbidity, 500 mg/L COD and 100 mg/L copper. Their subsequent study (Lai & Lin, 2004) focused on system performances and sludge characteristics. The study of Den & Huang (2005) demonstrated that electrocoagulation is effective at removing silica nanoparticles from CMP wastewater.

A more interesting study to treat copper CMP waste was reported by Ogden and co-workers (Stanley & Ogden, 2003). Copper was effectively removed from CMP waste by the treatment process shown in Fig. 2.1.

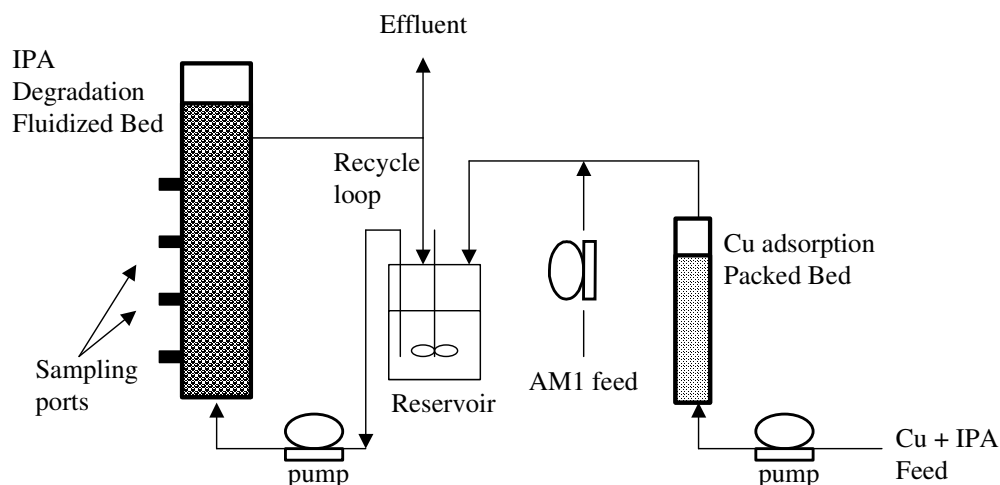


Fig. 2.1. Bioreactor configuration for removal of Cu and Organics from CMP wastewater (Ruiz & Ogden, 2004)

It was established that during the biotreatment stage, the presence of nanoparticles in the Cu-CMP wastewater can destroy the biosorbent sooner than acceptable for optimal performance. The motivation for this study is to explore dispersed multiphase-multicomponent interactions in the CMP wastewater and to develop a methodology for effective removal of both copper and alumino/silicate nanoparticles from CMP wastewater. The methodology will be based on a coagulation/filtration scheme involving a high-efficiency filtration and coagulation using chemical coagulant reagents based on aluminum and iron salts, natural coagulants and polyelectrolytes.

2.4. Chemical and Electrochemical treatments of CMP waste

Chemical mechanical planarization technique is being increasingly implemented in semiconductor elaboration with the consequent problem of waste production. Slurry waste treatment is attracting increasing attention to comply with environmental regulations and to

allow for recycling of deionized water, these slurries have to be treated to separate solids from the liquid dispersion medium.

To date most of the treatment methods combine conventional unit operations such as chemical precipitation/flocculation, micro and/or ultra-filtration, reverse osmosis and ion exchange (Mendicino *et al.*, 1999). Electrodialysis has also been recommended as a treatment option.

Electrocoagulation (i.e., electrochemical treatment) is considered an economical and efficient method for the treatment of wastewater that produces a minimum amount of dry sludge and does not require pH adjustment prior to treatment (Den & Huang, 2005). Concentration of colloidal suspensions has been reduced when an electrical current passes through suspension. It is employed to remove submicron-sized silica or alumina particles, reducing the particle content (monitored via turbidity measurements) and lowering the copper concentration in a single treatment (Lai & Lin, 2003). Electrocoagulation has also been used in conjunction with filtration to remove silica and suspended solids that tend to foul reverse osmosis membranes, thereby extending the life of the membranes (Pouet *et al.*, 1992).

Coagulation-flocculation followed by clarification by means of sedimentation, filtration or decantation, is the most widely used process for treating ‘difficult’ wastes from industries and even for domestic wastewaters. The process usually consists of the rapid dispersal of a coagulant into the waste with an intense agitation (rapid mixing) and followed by a slow agitation. Rapid mixing is needed to contact the coagulant with colloidal particles and reduce the electrostatic interparticle repulsion sufficiently so that the

Van der Waals attraction predominates, then allowing the particles to agglomerate. Kruilik *et al.* found that the treatment process of Golden *et al.* using proprietary polymer coagulant and microfiltration was also effective in removing copper ion (38 ppm to sub-0.1 ppm) from copper CMP wastewater that was previously readjusted to pH 7-8. Dispersants, stabilizers and surfactants can affect coagulation and flocculation treatment schemes, so careful attention to treatment chemistry is required.

Several existing technologies are available to treat metal bearing wastewaters. The simplest is conventional alkaline precipitation using caustic soda, lime or magnesium hydroxide. This process is inhibited by the presence of some complexing agents which keep the metal salts in solution. All of these processes use expensive chemical compounds which convert the metal to sludge and require dewatering and discarding. US. Patent No. 4,303,704 outlines a process that employs ion exchange resins with chelating groups to remove heavy metals from wastewaters in the presence of complexers or chelators. It seems that this resin with chelating groups would prefer heavy metals to sodium or a chelator and can take a metal away from its complexer.

Further studies are needed in order to understand coagulation of nanoparticles and to identify the most economic way to employ coagulation with current methodologies being studied including biotreatment of copper CMP wastes with the purpose of reducing contaminants in the effluent or exploring the possibility of water reuse in this process. Coagulation is an established technology for wastewater treatment. However, tuning of interfaces is needed in order to optimize its usage in the treatment of CMP wastes. Hence, further studies are needed.

CHAPTER 3: THEORETICAL BACKGROUND

3.1. Chemical Mechanical Planarization

Chemical mechanical planarization or chemical mechanical polishing, commonly abbreviated CMP, is a widely used technique in semiconductor fabrication for planarizing the top surface of an in-process semiconductor wafer or other substrate with the combination of chemical and mechanical forces.

The process uses abrasive nanoparticles and corrosive chemical slurry (commonly a colloid) in conjunction with a polishing pad and retaining ring, typically of a greater diameter than the wafer (Fig. 3.1). The pad and wafer are pressed together by a dynamic polishing head and held in place by a plastic retaining ring. The dynamic polishing head is rotated with different axes of rotation. This removes material and tends to even out any irregular topography, making the wafer flat or planar. This may be necessary in order to set up the wafer for the formation of additional circuit elements in order to bring the entire surface within the depth of field of a photolithography system, or to selectively remove material based on its position (Mc Aneny & Welty J., 2003).

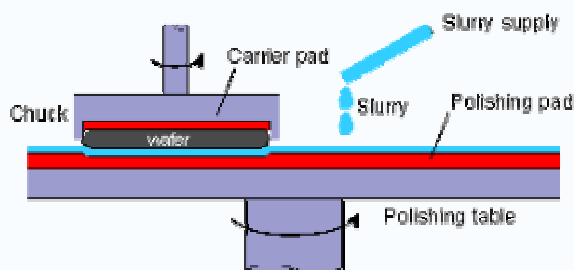


Fig. 3.1. Typical CMP polishing pad

The CMP procedure for the planarization of isolation layers of circuitry of modern chips was developed in the mid-80s at IBM. The introduction of CMP with the production of highly integrated circuits (i.e., processors) was a break-through for semiconductor industry leading to increased microchip performance, chip functionality, and a decrease in functionality cost.

Before about 1990 CMP was looked at as too "dirty" to be included in high-precision fabrication processes, since abrasion tends to create particles and the abrasives themselves are not without impurities. Since that time, the integrated circuit industry has moved from aluminum to copper conductors (Percy, 1998). Therefore this critical process is often termed Copper chemical mechanical planarization (Cu-CMP).

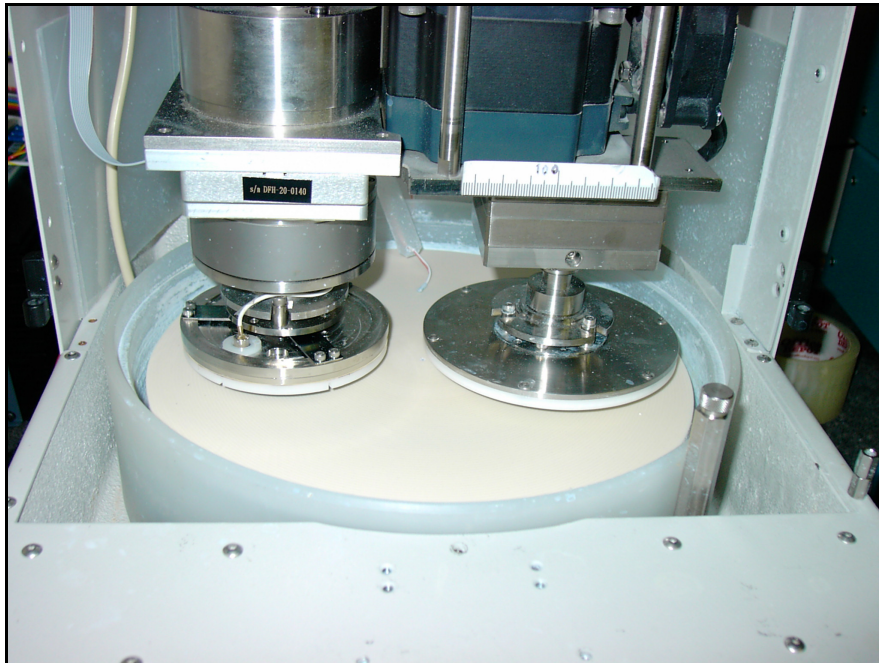


Fig. 3.2. CMP tool pad

3.1.1. CMP slurry

The CMP tool pad (Fig. 3.2) enables the transfer of mechanical forces to the wafer surface while CMP slurry provides both chemical action due to the slurry chemistry and polishing effects due to abrasives in the slurry. Cu-CMP process involves the mechanical abrasion of copper wafer surface and also the removal of abraded materials and its derivatives.

As it was mentioned in chapter 2, CMP slurry is composed of several compounds, most of which are proprietary. Its chemistry is relevant for the effectiveness of the process and is constantly varying with time, type of procedure and many other factors. It is basically composed of abrasive particles (alumina and silica), complexing agents, surfactants and corrosion inhibitors. Alumina and silica are used as abrasives but later will foul media during the biosorption treatment. Complexing agents such as citric acid prevent the formation of a precipitate and increase stability of the solution. Table 3.1 provides a guideline to prepare surrogate CMP slurry and includes the chemicals and their concentrations suggested by Siddiqui and co-workers (Siddiqui *et al.*, 2005).

Table 3.1. Guidelines to prepare surrogate Cu-CMP waste samples

Component	Concentration	Function
Alumina, α phase, 200 nm	1-2 % weight	Abrasive particles
Citric acid	1:1 mole ratio with copper	Complexing agent
Benzotriazole (BTA)	1:1 mole ratio with copper (II)	Corrosion inhibitor and complexing agent
Surfactant, non-ionic, anionic	1:1 mole ratio with copper (II)	Improve suspension of particles
Copper nitrate	10-40 ppm	

3.2. Fundamentals of colloidal chemistry

CMP slurry and wastes consists of a colloidal silica/alumina-based system, comprising a dispersion containing particles having a diameter within a range of 5 nm to 50 nm (nanometric scale) and a concentration within a range of 0.5% to 5% of weight.

In this system there is an interface between a solid and a liquid in which particles, in a finely divided state, are dispersed in a continuous medium. The particles are called the dispersed phase, and the medium in which they exist is called the dispersing phase (water). At this interface there is a transition region which shows properties differing from either of the two bulk phases (Minamihaba, 2005).

Colloidal systems may be classified by the affinity of the dispersed phase for the dispersing medium. If water is the dispersing medium, they are referred to as hydrophobic (water hating) and hydrophilic (water-loving). CMP colloidal slurry is defined as a hydrophobic system (Benefield *et al.*, 1982).

3.2.1. Surface charge on colloidal particles

An important factor in the stability of colloids is the presence of a surface charge. The sign of this charge (positive or negative) will depend on the nature of the material. Since like charges repel, similarly charged colloids are held apart from each other by electric charges and thus are prevented from aggregating into larger particles. This surface charge is developed most commonly through (Tchobanoglous *et al.*, 2002):

- i) Isomorphous replacement. Colloidal particle may acquire a charge through a replacement of ions in the lattice structure with ions from the solution (Fig. 3.3).

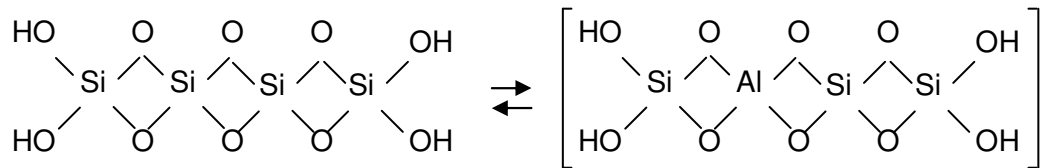


Fig. 3.3. Charge acquisition through isomorphous replacement of Al for Si

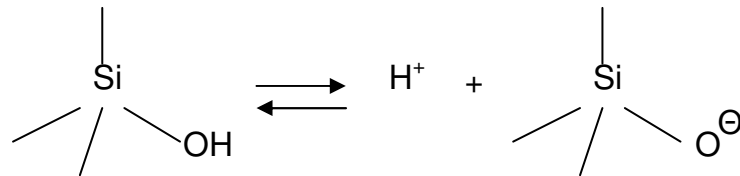
- ii) Structural imperfections. In clay and similar particles, charge development can occur because of broken bonds on the crystal edge and imperfections in the formation of the crystal.
- iii) Preferential adsorption. Many colloidal particles acquire a charge through the adsorption of certain ions on their surface. Oil droplets and gas bubbles adsorb anions (hydroxyl ions) and thus are negatively charged. Preferably anions are adsorbed because cations are generally more hydrated than anions.

- iv) Ionization of surface sites. In the case of substances such as proteins or microorganisms, surface charge is acquired through the ionization of carboxyl and amino groups.

An important difference between hydrophobic and hydrophilic colloids is that the former are stabilized almost exclusively by electrical repulsion forces, whereas the latter may be partly stabilized by particle solvation.

CMP slurry is basically composed of alumina/silica particles which cause turbidity in the dispersion, and are defined as hydrophobic particles.

Most particles in water, mineral and organic, have electrically charged surfaces, and the sign of the charge is usually negative. Since many silica particles (such as in CMP wastewater) are negatively charged at $\text{pH} \geq 6$, according to:



where $\text{pK}_a = 5.9$; therefore about half of the surface silica is negatively charged at $\text{pH } 5.9$.

3.2.2. Stability of colloids

The individual particles in a hydrophobic solid-in-liquid dispersion are acted upon by both repulsive and attractive forces. The most well-known repulsive force is caused by the interaction of the electrical double layers (EDL) of the surfaces (“electrostatic” stabilization as shown in Fig. 3.4). The most important attractive force is called the London-van der Waals

force which arises from spontaneous electrical and magnetic polarizations that create a fluctuating electromagnetic field within the particles and the space between them.

These two types of forces, repulsive and attractive, form the basis of the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory of colloid stability. Other forces include those associated with the hydration of ions at the surface (a repulsive force) and the presence of adsorbed polymers, which can cause either repulsion (“steric” interaction) or attraction (“polymer bridging”).

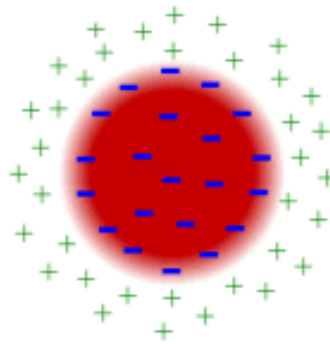


Fig. 3.4. Electrical double layer and distribution of charges in the vicinity of a colloidal particle

Colloidal particles in suspension are constantly moving due to Brownian motion. As two similarly charged particles approach each other, their diffuse counterion atmospheres (also known as EDL) begin to interfere and cause the particles to be repulsed. The repulsive energy between two particles, or the amount of work required to overcome this repulsion, decreases roughly exponentially with increasing particle separation as shown in Fig. 3.5.

The van der Waals' forces of attraction are due to universal attractive forces (called *dispersion forces*), first explained by London. The London-van der Waals' attractive energy of

interaction is inversely proportional to the second power of the distance separating the particles and thus decreases very rapidly with increasing intermolecular distance.

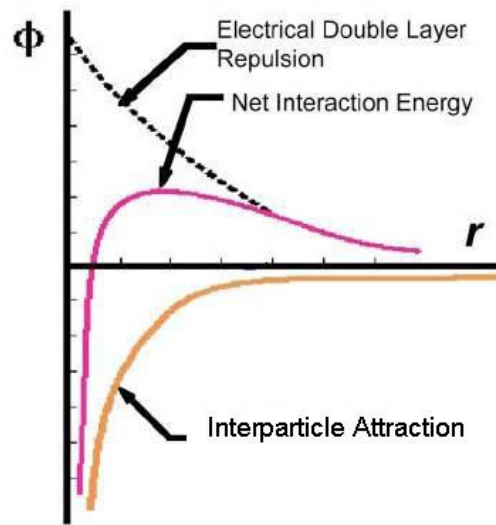


Fig. 3.5. Attractive and repulsive energies around dispersed nanoparticles as a function of particle separation

The repulsion and attraction curves can be combined to form a curve representing the resultant energy of interaction. This curve indicates that repulsion forces predominate at certain distances of separation, but that if the particles can be brought close enough together, the van der Waals' attractive forces will predominate and the particles will coalesce. To agglomerate, particles must possess enough kinetic energy to overcome the so-called energy hill on the total energy curve.

The forces stabilizing colloidal particles must be overcome and the individual particles must aggregate if they are to be separated from suspension. Aggregation can be brought about by the addition of selected chemicals, termed as *coagulants*, which overcome the stabilizing forces (Benefield *et al.*, 1982).

3.3. Mechanisms for colloid destabilization

Destabilization is the process in which the particles in a stable suspension are modified to increase their tendency to attach to one another and there is a reduction of surface potential. The aggregation of particles in a suspension after destabilization requires that they be transported toward one another.

To induce colloidal particles to aggregate, two distinct steps must occur:

- (1) The repulsion forces must be reduced; it means that the particles must be destabilized.
- (2) Particle transport must be achieved to provide contacts between the destabilized particles.

Particle destabilization can be achieved by four mechanisms: electrical double layer compression, adsorption and charge neutralization, adsorption and interparticle bridging and enmeshment in sweep floc (Benefield *et al.*, 1982; Tchobanoglous *et al.*, 2002). A brief description of these mechanisms follows.

3.3.1. Electrical double layer compression

It is a classical method for colloid destabilization achieved by the addition of ions having a charge opposite to that of the colloid which enter the diffuse layer surrounding the particle. To compress the double layer, a simple electrolyte such as NaCl is added to the suspension in sufficient amount. Coagulating power of cations increased in the ratio of 1:10:1000 as the valence of ions increased from 1 to 2 to 3. A similar observation for anions was noted by the Schulze-Hardy rule.

Two interesting aspects of double layer compression are: (1) the amount of electrolyte required to achieve coagulation is practically independent of the concentration of colloids in the dispersion (not stoichiometric); and (2) it is not possible to cause a charge reversal on a colloid, regardless of how much electrolyte is added (figure 3.6).

Destabilization by this mechanism is not a practical method for water treatment, because a high concentration of salt is required for destabilization and, in any case, the rate of particle aggregation would be relatively slow.

3.3.2. Adsorption and charge neutralization

This mechanism involves reducing the net surface charge of the particles in the suspension by means of the adsorption of coagulant compounds that carry a charge opposite to that of the colloids, and thus decreasing the thickness of the diffuse layer surrounding the particles and the energy required to move the particles into contact.

Destabilization by this mechanism differs from double layer compression in three very important ways. First, sorbable species are capable of destabilizing colloids at much lower dosages than nonsorbable, “double layer compressing” ions.

Secondly, destabilization by adsorption is stoichiometric because the required dosage of coagulant increases as the concentration of colloids increases.

Thirdly, an overdosing with adsorbable species may result in restabilization due to reversal of charge on the colloidal particles. It suggests that electrostatic repulsion effect can be outweighed in some cases with specific chemical interactions.

Hydrolyzed species of Al(III) and Fe(III) and polyelectrolytes can cause coagulation by adsorption as shown in figure 3.6.

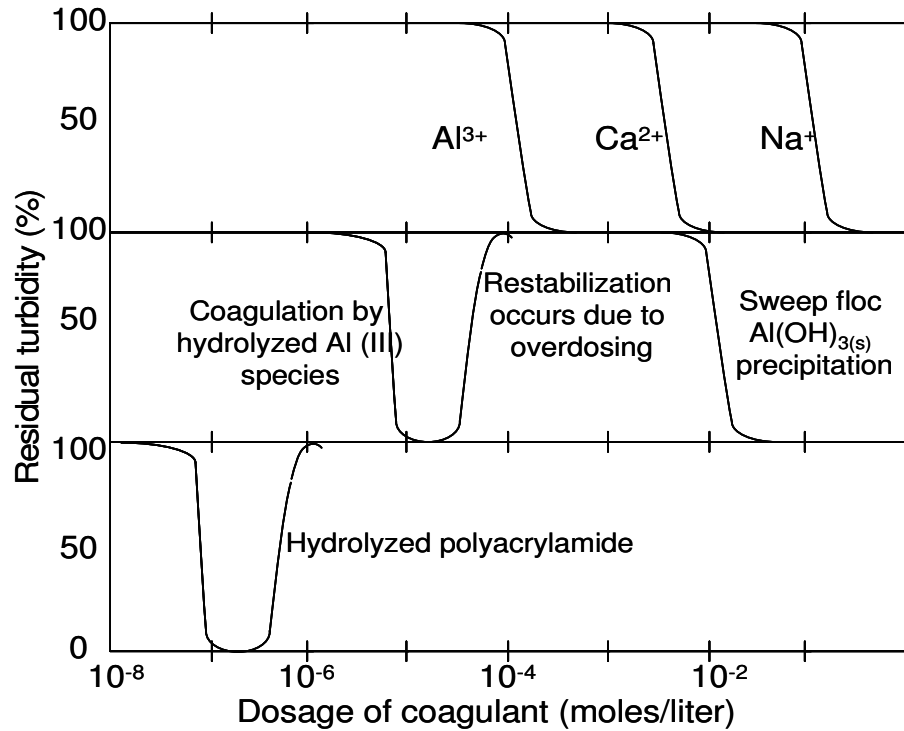


Fig. 3.6. Schematic coagulant curves for various modes of destabilization

3.3.3. Adsorption and interparticle bridging

Destabilization by bridging occurs when a polymer of a high molecular weight becomes attached at a number of adsorption sites to the surface of negatively charged particles along the polymer chain. The remainder of the polymer may remain extended into the solution and may adsorb on available surface sites of other particulates, thus creating a 'bridge' between the surfaces (as shown in pathways in Fig. 3.8). The polymer molecule must be long enough

to extend beyond the electrical double layer and the attaching particle must have available surface.

Since polymer bridging is an adsorption phenomenon, the optimum dose will generally be proportional to the concentration of particles present. Anionic, nonionic, and cationic polymers may function as bridging polymers due to high molecular weight and polymer size which increase the potential extent of bridging. Both positive (cationic) and negative (anionic) polymers are capable of destabilizing negatively charged colloidal particles under appropriate conditions.

The chemical bridging theory proposes that attachment may result from coulombic attraction if the particle and polymer are of opposite charge; or from ion exchange, hydrogen bonding, or van der Waals' forces if they are of similar charge. This bridging action results in the formation of a floc particle having favorable settling characteristics.

Inefficient coagulation may result from (as shown Fig. 3.8):

- i) an overdose of polymer or from intense or prolonged agitation.
- ii) a failed contact to another particles which may fold back and attach to other sites on the original surface, thus restabilizing the system.
- iii) an excessive addition of polymer so that the segments may saturate the surfaces of colloidal particles so that no sites are available for the formation of polymer bridges

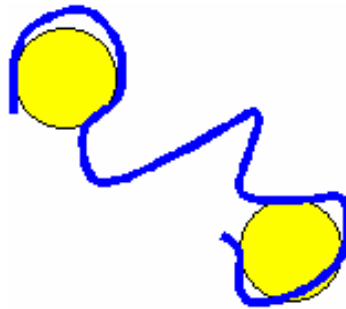


Fig. 3.7. Bridging flocculation. Polymer chains can ‘bridge’ particles to create larger masses that settle out

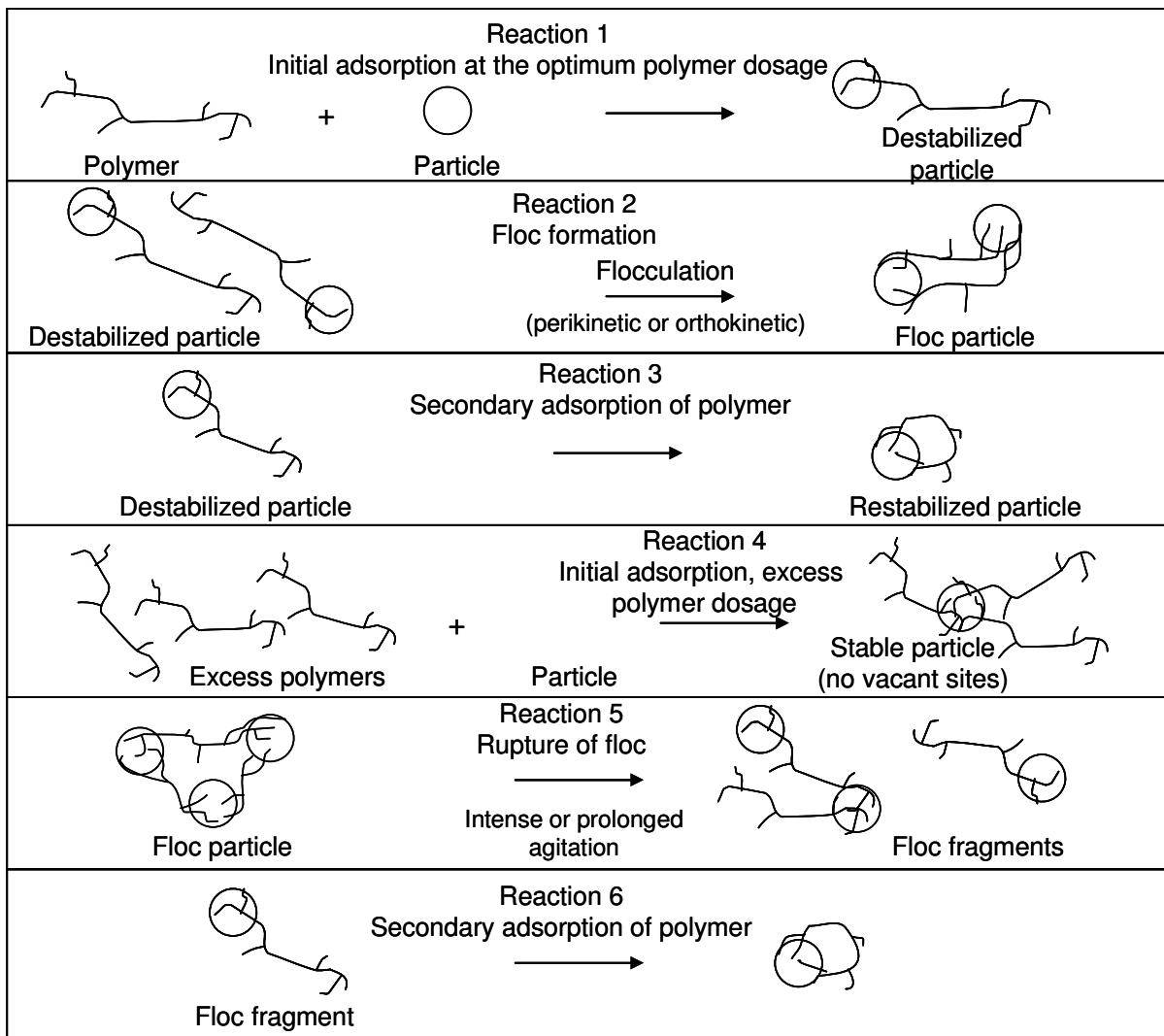


Fig. 3.8. Schematic of reactions between colloidal particles and polyelectrolytes

3.3.4. Enmeshment in sweep floc

Some soluble metal salts such as aluminum, iron or magnesium, hydrolyze and rapidly form an insoluble precipitate, thereby minimizing the concentration of ions added to the water. This type of destabilization has been described as an *enmeshment mechanism* or *sweep floc* in which finely divided particulates are entrapped in the amorphous precipitate formed. Nucleation of the precipitate may occur on the surface of particles, leading to the growth of an amorphous precipitate and the entrapment of particles in this amorphous structure as the precipitate settles.

Coagulants such as $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , MgCO_3 , and $\text{Ca}(\text{OH})_2$ can induce coagulation through the formation of insoluble $\text{Al}(\text{OH})_{3(s)}$, $\text{Fe}(\text{OH})_{3(s)}$, $\text{Mg}(\text{OH})_{2(s)}$, and $\text{CaCO}_{3(s)}$.

Sweep-floc coagulation distinguishes from double-layer compression and adsorption in the fact that there is an inverse relationship between the optimum coagulant dosage and the concentration of colloids to be removed. At low colloid concentrations a large excess of coagulant is required to produce a large amount of solid precipitate that will enmesh the relatively few colloidal particles as it settles. At high colloid concentrations, coagulation will occur at a lower chemical dosage because the colloids serve as nuclei to enhance precipitate formation.

3.4. Coagulation and flocculation in water treatment

Water treatment requires the removal of colloidal particles that remains in suspension causing turbidity, color and unacceptable conditions. Coagulation/flocculation is the most common process in water treatment and requires a unique combination of chemical and physical phenomena for producing particle destabilization followed by particle transport to promote collisions, between the destabilized particles. Destabilization is induced by the addition of a suitable chemical coagulant, and particle contact is ensured through appropriate mechanical mixing devices. If these collisions are successful, aggregation occurs.

3.4.1. Coagulation

Coagulation is a complex process, involving many reactions and mass transfer steps. The process is essentially three separate and sequential steps: coagulant formation (where applicable), particle destabilization and interparticle collisions. In situ coagulant formation and particle destabilization occur during and immediately after chemical dispersal and involve a rapid initial mixing stage over a short time frame (usually less than 1 min). Whilst interparticle collisions that cause aggregate (microfloc) formation begin during rapid mixing but predominantly occur in the flocculation process (Tchobanoglous *et al.*, 2002).

Essentially this is a process of destabilization and reduction of the surface charge on suspended particulates and colloids, and to lessen the repelling character of the particles and allow them to become attached to other particles so they may be removed in subsequent processes.

For example, using the aluminum sulfate salt known as alum $[\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}]$ in coagulation involves formation of an assortment of chemical species, called aluminum hydrolysis products, that cause coagulation, and are formed during and after the time that alum is mixed with the water to be treated.

3.4.2. Flocculation

The term ‘flocculation’ is used to describe the process whereby the size of aggregated particles (microflocs) increases as a result of physical interparticle contacts.

The purpose of flocculation is to form large, dense and rapid-settling flocs from finely aggregated particles and chemically destabilized particles which were previously formed in the coagulation step. Then these larger particles can be removed readily by sedimentation or filtration.

Flocculation typically follows rapid mixing where chemical have been added to destabilize the colloidal particles, and involves less intense mixing of the particulates over a prolonged period of time (approximately 5-30min) to increase the rate of encounters or collisions without breaking the formed flocs.

There are two types of flocculation: (1) microflocculation and (2) macroflocculation. The distinction between these two kinds of flocculation is based on the particle sizes involved.

Microflocculation (also known as perikinetic flocculation) is referred to the aggregation of particles brought about by the random thermal motion of fluid molecules. The random thermal motion of fluid molecules is also known as *Brownian motion* or *movement* (see figure 3.9a). Microflocculation has significant influence on transport of particles that are in the size range from 0.001 to about 1 μm .

Macroflocculation (also known as orthokinetic flocculation) is referred to the aggregation of particles greater than 1 or 2 μm . Macroflocculation can be brought about together (flocculated) by:

- i) Induced velocity gradients (see Fig. 3.9b). Faster moving-particles will overtake slower-moving particles in a velocity field. If the particles that collide stick together, a larger particle will be formed that will be easier to remove by gravity separation.
- ii) Differential settling (see Fig. 3.9b). Large particles overtake smaller particles during gravity settling. When two particles collide and stick together, a larger particle is formed that settles at a rate that is greater than that of the larger particle before the two particles collided.

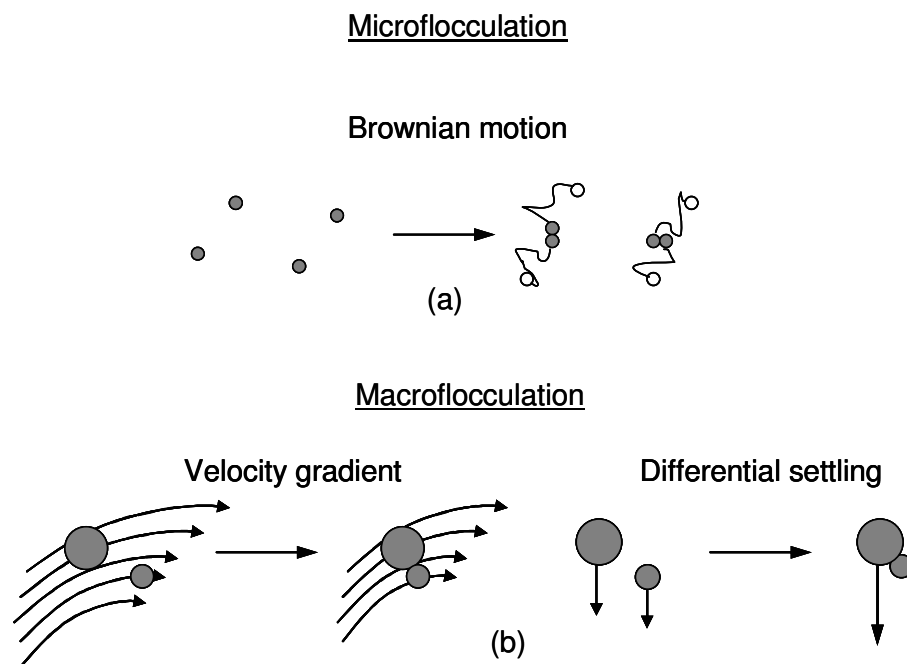


Fig. 3.9. Illustration of the two types of flocculation: (a) microflocculation; and (b) macroflocculation due to (i) fluid shear and (ii) differential settling

3.4.3. Coagulants and flocculants in water treatment

The chemicals used to destabilize colloids are known as coagulants or flocculants, depending on their mode of operation.

There is a distinction between them: a *coagulant* is a chemical used to initially destabilize the suspension and is typically added in the rapid-mix process; and a *flocculant*, in most cases, is used after the addition of a coagulant, its purpose is to enhance floc formation and to increase the strength of the floc structure.

In any case, depending on how and where it is used and at what dosage, a coagulant is sometimes a flocculant and vice versa. In this research, no distinction is made between coagulants and flocculants and the term “coagulant” is used exclusively.

There are three types of coagulants:

(1) Inorganic coagulants

The two principal inorganic coagulants used in wastewater treatment are salts of aluminum and ferric ions. Both Al(III) and Fe(III) are hydrolyzing metal ions with a complex aqueous chemistry that will dissociate to yield trivalent Al^{3+} or Fe^{3+} ions and hydrate to form the aquometal complexes $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. These complexes pass through a series of hydrolytic reactions forming mononuclear species such as $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$; and polynuclear species such as $\text{Al}_{13}(\text{OH})_{34}^{5+}$. These positively charged species adsorb very strongly onto the surface of most negative colloids.

The hydrolysis products, not the aluminum ions, cause particulate destabilization through adsorption and charge neutralization.

The most commonly used inorganic coagulants are listed in Table 3.2.

Table 3.2. Common water treatment inorganic coagulants

Chemical Name	Formula	Molecular weight	Common color and form
Aluminum sulfate (alum)	$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	594.4	Tan to gray green: powder granules, liquid and lump
Ferric sulfate	$\text{Fe}_2(\text{SO}_4)_3$	399.9	Dyhydrate: red-brown granules Trihydrate: red-gray granules
Ferric chloride	FeCl_3	162.2	Anhydrous: green-black powder Heptahydrate: yellow-brown lump Liquid: dark-brown solution

(2) Organic coagulants

Organic coagulants are long-chain polymers consisting of repeating chemical units with a structure designed to provide distinctive physicochemical properties to the polymer. The chemical units usually have an ionic nature that imparts an electrical charge to the polymer chain. Hence, synthetic organic polymers are often termed *polyelectrolytes*.

They have two principal objectives in water treatment: destabilization of particles (through complex interactions) and formation of larger and more shear-resistant flocs. Destabilization occurs primarily through charge neutralization and polymer bridging. Organic polymers are used as primary coagulants, coagulant or filter aids, and sludge conditioning.

According to the ionizable groups and charge they acquire, there are three types of polyelectrolytes (see Table 3.3): cationic (positive charge), anionic (negative charge) and nonionic (no ionic charge).

Table 3.3. Some synthetic organic polymers used as coagulants

Type	Chemical Name	Formula	Molecular weight
Cationic	Polyaluminum chloride	$Al_n(OH)_mCl_{3n-m}$	10^4-10^6
Anionic	Hydrolyzed polyacrylamide	$\left[\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2\text{CH} \\ \qquad \qquad \\ \text{C=O} \qquad \text{C=O} \\ \qquad \qquad \\ \text{NH}_2 \qquad \text{ONa} \end{array} \right]_n$	10^4-10^7
Nonionic	Polyacrylamide	$\left[\begin{array}{c} \text{CH}_2 - \text{CH} \\ \\ \text{C=O} \\ \\ \text{NH}_2 \end{array} \right]_n$	10^5-10^7

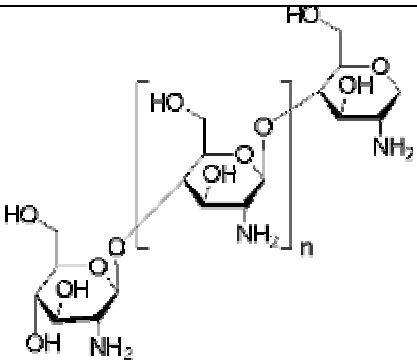
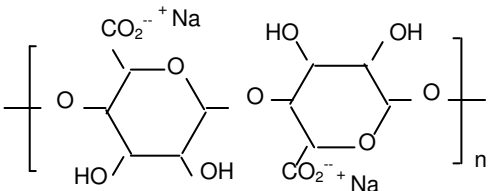
(3) Natural coagulants

Coagulants made from natural organic compounds are sometimes used for water treatment. Natural coagulants such as chitosan (cationic) and sodium alginate (anionic) are not only as effective as or even more effective than their synthetic polyelectrolytes counterparts at similar dosages but they also do not cause any adverse effects to human health.

As organic coagulants, they produce a lower volume of sludge compared with alum flocculation and their effectiveness is not much affected by the pH level of water.

Natural coagulants, which can be extracted from certain kinds of plant and animal life, are a workable alternative to synthetic polyelectrolytes (Kawamura,1991).

Table 3.4. Common water treatment natural coagulants

Type	Chemical Name	Average Molecular weight	Formula
Cationic	Chitosan	$\sim 10^6$	
Anionic	Sodium alginate	2.59×10^5	

CHAPTER 4: EXPERIMENTAL PROCEDURES

4.1. Experimental methodologies

A combination of experimental setups was utilized. These setups included jar tests, flask/beaker tests, turbidity measurements, filter test setups, dilution studies, and particle content experiments. Flask/beaker tests were used to dilute the CMP slurry and coagulants (if they are to be in solution) and beakers were also used in the jar test procedure. Whatman filters were used to enhance removal of large conglomerate of particles (flocs) from treated CMP waste containing coagulant.

The most important tasks of this study included:

- (i) Sample preparation and characterization of CMP wastewater;
- (ii) CMP waste coagulation and filtration;
- (iii) CMP waste dilution and its behavior with successive dilutions;
- (iv) Evaluation of synthetic organic polymers, a natural coagulant and inorganic coagulants;
- (v) Determination of most effective coagulant and optimal operating conditions such as coagulant dosage, pH, and suspension turbidity; and
- (vi) Turbidity reduction and suspended solids removal by coagulation and coagulation/filtration

4.2. Procedures for sample preparation and characterization of CMP wastewater

Three different kinds of samples were used:

(1) Surrogate CMP waste sample; (2) Commercial CMP slurry; and (3) CMP wastewater obtained from the University of Arizona tool room.

These three types of CMP samples were used in studies of coagulation and/or coagulation/filtration as well as nanoparticle-copper or nanoparticle-coagulant interactions in these effluents and how they influence the performance of treatment schemes. It was important to understand the slurry chemistry and the way it affected copper and particle removal from CMP wastes. The tendency of copper ions to partition themselves between the particles and liquid was studied after coagulation process taking into account turbidity reduction and comparing with samples without copper in solution.

Water quality analyses were conducted on all influent and effluent samples on coagulation/filtration process. Standard EPA test methods were used in physicochemical analysis.

4.2.1. Commercial CMP slurry

CMP wastes samples were prepared from commercially procured iCue[®] 5001 slurry obtained from Cabot Microelectronics (Wisconsin, USA). The raw slurry and different dilutions made of this slurry were characterized according to: turbidity, total solids and characteristics, and pH. Fresh CMP slurries in dilution did not contain copper II ions, so a

standard cupric nitrate hydrate solution (Cu^{2+}) was added to these diluted samples in order to formulate different concentrations of this ion in the Cu-CMP waste samples.

Since it was known from prior studies (including Corlett, 2000; Golden *et al.*, 2000; Stanley & Ogden, 2003), that polishing slurry from CMP processes consisted of 5-10% of very fine particles (nanometer to micrometer size scale), the raw procured slurry was diluted accordingly by using the prepared copper solutions taking into consideration that these ions tended to distribute between solid and liquid phase.

At the same time, there were two types of commercial CMP slurries: alumina-based and silica-based CMP wastes. Commercial alumina CMP slurry was mainly used during experimental procedures. Therefore, for the purpose of this research, the term ‘commercial CMP slurry’ is used for alumina-based slurries.

Procedure for preparing commercial CMP waste samples:

The procedures followed to prepare waste samples from commercial CMP slurry and to prepare copper solutions are given below.

I) Preparation of CMP waste dilutions:

- Dilute commercially available alumina-based CMP slurry (iCue[®] 5001, Cabot Microelectronics Corp., USA) with deionized water.
- Obtain a waste sample of 500 mL, yielding suspension turbidities of approximately 200 and 900 NTU.
- Analyze three equal samples of these solutions to determine total solids (TS) with gravimetric method EPA 160.3 and measure turbidity (in NTU) with a turbidimeter.

II) Preparation of Cu-CMP waste samples

- Add about 2.95 g of crystal $\text{Cu}(\text{NO}_3)_2$ hydrated (Sigma-Aldrich, 99.999% purity grade) to 1L of deionized water using a volumetric flask to obtain a 1000 ppm Cu(II) aqueous solution.
- Add this copper solution to 500 mL of commercial CMP slurry (previously diluted) and obtain a Cu (II) concentration within a range of 50-200 ppm.
- Analyze three equal samples of these solutions to determine total solids (TS) with gravimetric method EPA 160.3 and to measure turbidity (in NTU) with a turbidimeter.

After these preparation steps, coagulation procedures were performed with different coagulants to observe how they removed solids from suspensions without copper, and how copper influenced the removal of turbidity and subsequent particle reduction in copper CMP solutions. That gave some idea about the distribution of Cu^{2+} ions between the clear liquid and settled particles, how it formed complex compounds with silica and alumina nanoparticles and how it interacted with chemical coagulants during coagulation/flocculation process. On the other hand, dilutions without copper gave some understanding about the interactions among nanoparticles and coagulants, and how a greater turbidity or different pH influenced in the amount of coagulant required.

4.2.2. Surrogate Cu-CMP waste sample

Surrogate samples were prepared from procured laboratory chemicals and materials. From literature, it is known that CMP wastewater is basically composed of abrasive nanoparticles, copper (II) ions, pH buffers (such as citric acid), corrosion inhibitors and surfactants. As it was mentioned in chapter 3, the surrogate slurry was prepared according to the indications given by Dr. Junaid A. Siddiqui.

Table 4.1. Preparation of surrogate Cu-CMP waste sample

Chemical Name	Concentration
Alumina, α phase, 200 nm	1-2 % weight
Citric acid	1:1 mole ratio with Cu^{2+}
Benzotriazole (BTA)	1:1 mole ratio with Cu^{2+}
Surfactant, non-ionic, anionic	1:1 mole ratio with Cu^{2+}
Copper nitrate	10-40 ppm

Procedure for preparing surrogate Cu-CMP waste samples:

The following procedures were performed to prepare surrogate Cu-CMP waste samples from chemical reagents:

- First, prepare a stock solution of copper (II) ions by adding about 2.95 g of crystal cupric nitrate hydrated, $\text{Cu}(\text{NO}_3)_2(\text{s})$ (Sigma Aldrich, 99.999% purity grade), to 1 L of deionized water in a volumetric flask to obtain a 1000 ppm $\text{Cu}(\text{II})$ solution.

- From this stock solution, prepare 1 L of 10-40 ppm copper concentration using deionized water as water supply and mix thoroughly with a magnetic stirrer.
- Add the other components to form the surrogate slurry and continue mixing until the solution is completely homogeneous.

An attempt was also made to characterize the sample according to total solids (TS), pH, turbidity and settling characteristics of particles.

4.2.3. Cu-CMP samples from microelectronics industry

These samples were obtained from the University of Arizona tool room. The raw CMP waste was characterized to determine copper content (ICP-MS), turbidity (EPA method 180.1 as described in Appendix B), total solids (EPA method 160.3 as described in Appendix A) and pH. Coagulation procedures were carried out using different chemical coagulants. Turbidity reduction as well as solid removal was studied.

4.3. Procedures and experimental setups for CMP waste coagulation and filtration

Three types of coagulation experiments were conducted. Most of them were performed using alumina-based commercial CMP slurry (that was accordingly diluted) as the wastewater to be analyzed. The amount of removed suspended solids was dependent on the coagulant type and dosage. In this procedure, optimal coagulant dosage, pH and suspension turbidity were looked for as well as the most effective coagulants.

The second type of experiment involved the usage of surrogate laboratory Cu-CMP waste samples whose main objective was to investigate the reduction of copper concentration and solids in suspension by means of coagulation process using the most effective coagulants.

The third type involved the usage of Cu-CMP from the University of Arizona tool room. In the same way that surrogate Cu-CMP, coagulation process was performed using the most suitable coagulants.

4.3.1. Equipment and instruments

For coagulation experiments the following materials were utilized:

- 1 Phipps & Bird six-paddle stirrer 7790-400
- 1 Turbidity Meter LaMotte 2020 e/i
- 1 pH meter Orion 410A with buffer solutions (pH 4, 7 and 10 from Fisher Scientific)
- 1 electronic laboratory balance Mettler Toledo AG135
- 6 graduated beakers, 1000 mL
- 2 glass beakers, 300 mL
- 1 glass measuring pipette, 10 mL
- 3 micropipettes Eppendorf; 10 μ L, 100 μ L and 1000 μ L
- 1 macropipette, 5 mL
- 1 graduated measuring cylinder, 1000 mL
- 1 stopwatch

- Also six evaporating basins, pipette tips (10 μ L, 100 μ L and 5 mL), two droppers, rods, and aluminum weighing dishes

For filtration procedures were also included:

- 2 glass filtering flasks, 500 mL
- 2 ceramic Buchner funnels, 10 cm diameter
- Filter paper Whatman # 2 Qualitative (8 μ m), 12.5 cm
- Filter paper Whatman # 50 Hardened (2.7 μ m), 12.5 cm

For preparation of coagulant solutions (if applicable) and acid/basic solutions:

- 1 volumetric flask, 1000 mL
- 1 magnetic stirrer Thermolyne Nuova II

4.3.2. Chemical reagents and others

For coagulation procedures:

- Deionized water
- Aluminum sulfate octadecahydrate >98%, inorganic coagulant, Sigma-Aldrich
- Ferric sulfate hydrate 97%, inorganic coagulant, Sigma-Aldrich
- Chitosan (from crab shells) practical grade, natural coagulant, Sigma-Aldrich
- Polyacrylamide, average MW ~10,000, nonionic polymer, Sigma-Aldrich
- Hydrolized polyacrylamide, anionic polymer

To adjust pH, diluted acid/basic solutions were prepared from:

- Sodium hydroxide solution 0.05 N, Ricca Chemical Company.

- Nitric acid 50% (v/v) aqueous solution, Ricca Chemical Company.

To prepare a chitosan acid dilution it was used:

- Acetic acid glacial 99.9% weight, Fisher Chemical

To prepare surrogate CMP waste it was necessary:

- Copper (II) nitrate hydrated, 99.999%, Sigma-Aldrich
- Aluminum silicate particles 0.2-8.0 μm , Duke Scientific Corp.
- Citric acid 99%, Sigma Aldrich
- Benzotriazole 99%, Sigma-Aldrich
- Triton X-100, <3% polyethyleneglycol, Sigma-Aldrich

4.3.3. Jar Test technique

Jar Test is a common laboratory procedure used to determine the optimum operating conditions for water or wastewater treatment. This method allows adjustments in pH, variations in coagulant or polymer dose, alternating mixing speeds, and testing of different coagulant or polymer types, on a small scale. Jar test simulates the coagulation and flocculation processes that encourage the removal of suspended colloids and organic matter which can lead to turbidity problems, followed by gravity settling. It is the quickest and most economical way to obtain good reliable data on the many variables which affect the coagulation and solid removal process.

The amount or dosage of coagulant required to precipitate and remove metals and nanoparticles in Cu-CMP slurries was not only dependent on the concentration of such

components in solution, but also on other factors. In order to optimize the coagulation process, the following parameters were considered:

- Coagulant dosage
- Solution pH
- Type of coagulants used
- Presence of inorganic and organic contaminants: dispersants, stabilizers and surfactants (Golden *et al.*, 2000).
- Possible sequence in which coagulants were added and chemicals used to adjust pH.

4.3.3.1. Jar Test procedure

CMP waste contains ingredients other than dissolved metals and alumina-silicate particles that may have affected the treatment methodology. Therefore, this procedure provided a starting point and some adjustments were required to achieve the desired results.

Note: One container was used as a control (its properties remained invariable during this procedure in order to make comparisons). The other ones were adjusted depending on what conditions were tested. For instance, the solution pH and suspension turbidity were fixed and different amounts of coagulant were added in order to determine optimum coagulant dosage taking into account the best turbidity removal.

The jar test procedure involved the following steps:

- Add 500 mL of CMP waste sample to the jar testing apparatus (containers/beakers).
- Mix thoroughly until complete homogeneity, measure initial turbidity and fix pH for all samples.
- Add different amounts of coagulant to each container and rapidly mix at 100 rpm for 1 min.
- Reduce stirring speed to 25 rpm and continue mixing for 30 min.
- If necessary, adjust pH (only for inorganic coagulants which are pH dependent).
- Turn off the mixer and allow the samples to settle down for 30 min.
- Determine an approximate time when a phase separation occurs
- Take a 10 mL sample of the clear solution to half from the height of the container
- Measure the final turbidity for each sample.
- Graph percentage residual turbidity versus coagulant dosage and determine the optimum dosage.

This procedure was established to determine the optimal dosage of coagulant at a certain conditions such as pH and initial turbidity, but changing these parameters another optimal dosage was found. Hence, comparing results, optimum coagulant dosage, suspension

turbidity and pH of coagulation were established for a specific coagulant taking into account the best removal of solids. Same procedure was then followed for the other coagulants

4.3.4. Coagulation/filtration experiments

The experiments to conduct coagulation/filtration tests were performed in the same manner as the jar test procedure but with some variations following these steps:

- Add 500 mL of CMP waste sample to the jar testing apparatus (containers/beakers).
- Mix thoroughly until complete homogeneity, measure initial turbidity and fix to the optimum pH
- Add the optimum coagulant dosage to each sample and rapidly mix at 100 rpm for 1 min.
- Reduce stirring speed to 25 rpm and continue mixing for 30 min.
- If necessary, adjust pH (only for inorganic coagulants which are pH dependent).
- Turn off the mixer
- Filtrate samples in a vacuum Buchner funnel using different types (pore size) of filter papers
- Take a 10 mL sample of the filtered solution
- Measure the final turbidity for each sample

4.4. CMP waste studies

Experiments related to coagulation of Cu-CMP wastes basically focused on:

- i) Evaluation of the salts of Al (III) and Fe (III) salts, synthetic polymers and chitosan as coagulants to reduce nanoparticles concentration in CMP wastes;
- ii) Determination of the optimal coagulant dosage, pH and suspension turbidity;
- iii) Adsorption studies on filter media; and
- iv) Optimization of removal of nanoparticles which would foul media during biotreatment experiments.

Due to changing conditions from slurry to slurry, additionally some other experiments were performed with the purpose of determining how this wastewater behaved with successive dilutions and studying how total solids and turbidity varied with CMP volume added to the dilution (% vol CMP).

Characterization of diluted CMP waste samples

As it was mentioned, different diluted CMP samples were obtained and yielded turbidities within a range of approximately 200 to 900 NTU following these guidelines:

- Obtain 500 mL CMP waste sample diluting 5 mL of a specific commercial CMP slurry with deionized water in a 1000 mL beaker
- Mix thoroughly until complete homogeneity
- Measure turbidity, pH and total solids

Repeat first step adding 10 mL of CMP slurry, 15mL, 20 mL and so on, then continue next steps. Finally, graph turbidity versus % volume CMP and turbidity versus TSS.

Successive dilutions

The following procedure had as objective to study the deviation from theoretical behavior (in terms of turbidity and total solids) of real successively diluted samples.

- Prepare 500 mL of a sample with 800 NTU turbidity
- Measure turbidity, pH and total solids
- Take 250 mL of this solution and dilute with 250 mL of deionized water
- Mix thoroughly until complete homogeneity
- Measure turbidity, pH and total solids
- Then, take 250 mL of this new solution and dilute with 250 mL of deionized water and measure the same parameters aforementioned
- Repeat the above mentioned steps until a 50 NTU turbidity is obtained

Theoretically first sample is 800 NTU; the second one should be 400 NTU; third one with 200 NTU, and so on.

CHAPTER 5: RESULTS AND DISCUSSION

The experiments conducted in this research were performed with commercial iCue[®] 5001 CMP slurry obtained from Cabot Microelectronics in order to determine parameters such as chemical coagulation to find optimal coagulant dosage, pH and initial suspension turbidity. Then, with these optimal results, a comparison was made with other types of CMP slurries and copper based CMP wastes, and how turbidity removal could be enhanced by means of filtration tests. Finally, some coagulants were recommended for treating CMP wastes by comparing percentages of residual turbidity remaining in treated wastewater.

5.1. Characterization of CMP wastes

Before developing the studies to treat chemically wastewaters generated during CMP process, some preliminary studies were carried out using commercial CMP slurry with the purpose of studying its characteristics and complexity, and understanding the behavior of this suspension when it is diluted with deionized water and when successive dilutions were made from a sample of known turbidity.

5.1.1. CMP wastewater properties

Table 5.1 lists the main characteristics of some CMP slurries and copper CMP slurry obtained from the University of Arizona toolroom.

Commercial CMP slurry (alumina-based suspension), silica CMP slurry, surrogate CMP waste, Cu-CMP wastewater (University of Arizona tool room), and commercial Cu-CMP wastewater (prepared from commercial CMP slurry and 1000 ppm copper solution) were characterized.

Commercial CMP slurry mostly contained fine oxide particles mainly aluminum oxide (alumina, Al_2O_3) and had a milky color. Silica CMP slurry was composed of fine suspended oxide particles mainly silicon dioxide (silica, SiO_2), and had a milky appearance. Surrogate CMP waste prepared from procured laboratory chemicals (as indicated in table 4.1) had a clearer appearance and consequently a low turbidity but contained alumino-silicate nanoparticles. Cu-CMP of University of Arizona tool room was different from the other samples, and had a faint blue and milky color which indicated the presence of copper in solution and fine suspended oxide particles.

Table 5.1. Characteristics of CMP wastes

	Comm. CMP slurry	Silica CMP slurry	Surrogate CMP slurry	Cu-CMP waste (UofA tool room)
Oxide particles	Al_2O_3	SiO_2	$\text{Al}_2\text{O}_3\text{-SiO}_2$	SiO_2
pH	8.32	8.66	6.88	7.78
TS (mg/L)	54480	380130	67130	5050
Turbidity (NTU)	>13500	1200	70	240
Copper (ppm)	-	-	20	185-190
Density (g/mL)	1.02	1.20	0.99	1.00
Color	Milky	Milky	Colorless	Faint blue

Commercial and silica CMP slurries had high total solids (TS) contents of 54480 and 380130 mg/L, respectively, being much higher than 5050 mg/L of Cu-CMP waste (UofA tool room). This significant difference was due to the dilution of the CMP slurries with ultra purified water (UPW) and streams that contain organic compounds during wafer washing and cleaning of CMP process. The lower turbidity of Cu-CMP waste (240 NTU), as compared to that of commercial CMP slurry (>13500 NTU) and silica CMP slurry (1200 NTU) was also due to the fact that slurries were diluted during the polishing procedure.

After wafer cleaning and polishing to reduce wafer topological imperfections, CMP slurries dragged copper ions and some organic compounds. For this reason, there was no copper content in original slurries and this distinguishes it from the Cu-CMP waste (as illustrated in Fig. 5.1). Also this practice slightly reduced pH of the suspensions.

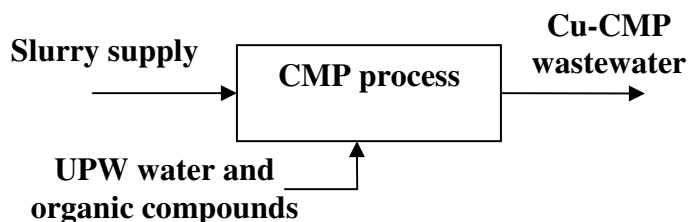


Fig. 5.1. Schematic diagram of CMP process

Characteristics of the surrogate CMP waste approximated to those of silica and alumina CMP wastewaters.

5.1.2. Dilution of CMP slurry

Before chemical coagulation process, it was essential to know the preparation of CMP waste samples by means of dilution of the original slurry with deionized water within a range of 1% to 6% vol., and yielding suspension turbidities of approximately 200-900 NTU.

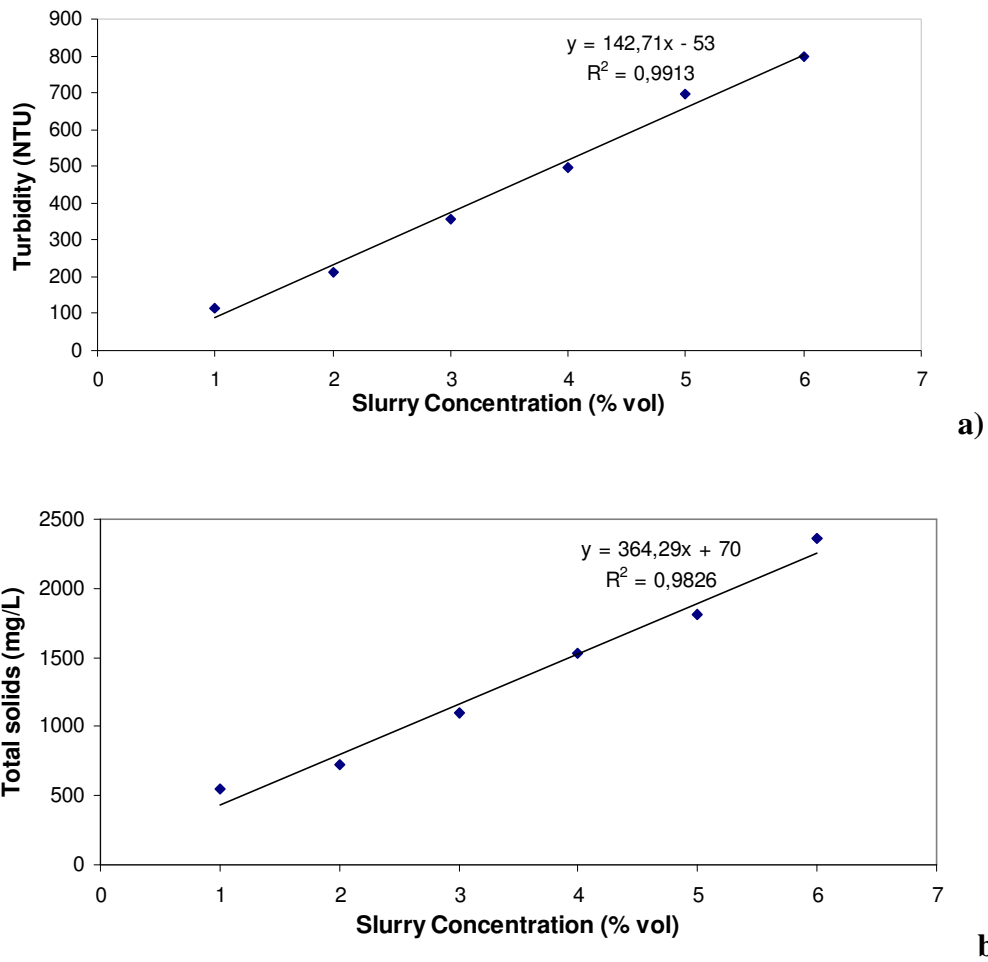


Fig. 5.2. Variations of turbidity (a) and total solids (b) with dilutions of slurry for preparation of CMP waste samples

The turbidity and total solids of the alumina suspension exhibited a linear relationship with the slurry dilution levels for slurry concentration less than 6% vol. as shown in Fig. 5.2.

In this way, CMP waste samples of a desired turbidity were prepared to conduct experimental tests.

Successive dilutions

Some experiments were performed in order to investigate if there was any deviation from the ideal turbidity when CMP samples were sequentially diluted.

For this purpose, successive dilutions 1:1 from a sample of 800 NTU were made. Theoretically first sample has turbidity of 800 NTU; the second one has 400 NTU; third one 200 NTU, and so on. Standard deviations were 0.0, 7.8, 2.1, 0.0 and 0.4 for each level of dilution respectively.

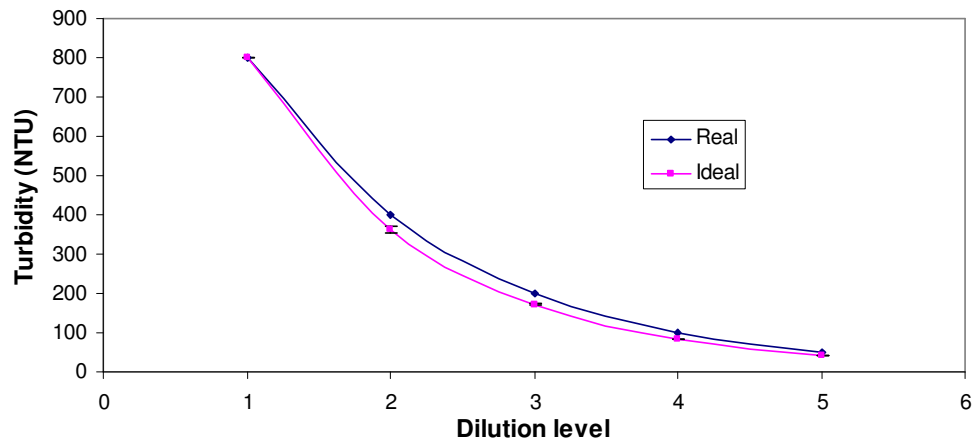


Fig. 5.3. Deviation from the ideal turbidity for successively diluted commercial CMP slurry

As it was observed in Fig. 5.3, there was a minor difference between the values obtained experimentally (real) and the ones that were supposed to be obtained (theoretically). It should

be noted that all samples were vigorously stirred before the measurements in order to achieve homogeneity.

5.2. Chemical coagulation experiments

In the chemical coagulation process, the nano-sized suspended particles were first aggregated by the addition of chemical coagulants (coagulation step) and then, the aggregated particles formed large, dense and rapid-settling flocs during flocculation step.

The mixing conditions were provided with 1 min rapid mixing (100 rpm), followed by 30 min slow mixing (25 rpm). Sedimentation was allowed to occur for 30 min, and the residual turbidity of the supernatant was measured.

Since it was difficult to reproduce the initial turbidity for CMP waste samples, instead of turbidity, the results were treated in terms of percentage of residual turbidity which was used to represent the amount of nanoparticles present in suspension with respect to the initial amount of original sample before coagulation.

$$\% \text{ Residual turbidity} = 100 - \frac{\text{Initial turbidity} - \text{Final turbidity}}{\text{Initial turbidity}} \times 100 \%$$

The following chemical coagulants were used: two inorganic coagulants (aluminum sulfate and ferric sulfate), one natural cationic coagulant (chitosan) and two polyelectrolytes such as a nonionic coagulant (polyacrylamide) and an anionic polymer.

To determine the lowest coagulant dosage at the minimum value of residual turbidity, a graph of percentage of residual turbidity versus coagulant dosage was constructed for each coagulant. These experiments were conducted with alumina-based commercial CMP slurry.

Previous experiments (Ihnfeldt & Talbot, 2006) demonstrated that between pH values 6.5 and 9.5 the alumina is negatively charged owing to the measured isoelectric point (IEP) of the Cabot alumina slurry being pH ~6.5 whereas the IEP of α -alumina has been published as 9.2 in an aqueous dispersion. It means that at low pH values (less than 6.5), alumina particles are positively charged in the slurry.

The pH of the slurry had the largest effect on the particle surface charge (commonly measured as zeta potential), agglomerate size and interactions between coagulant-nanoparticles. That was a relevant factor to effectively remove particles from slurry as well as the electrical charge. The coagulant and hydrolysis products (in the case of inorganic coagulants) played an important role to engulf alumina nanoparticles.

i) Aluminum sulfate (alum)

Alum, an inorganic coagulant and widely used in water treatment, effectively removed nano-sized particles at pH=5.0, 100 mg/L dosage and initial suspension turbidity of approximately 900 NTU with percentage residual turbidity (% R.T.) of 0.79 %.

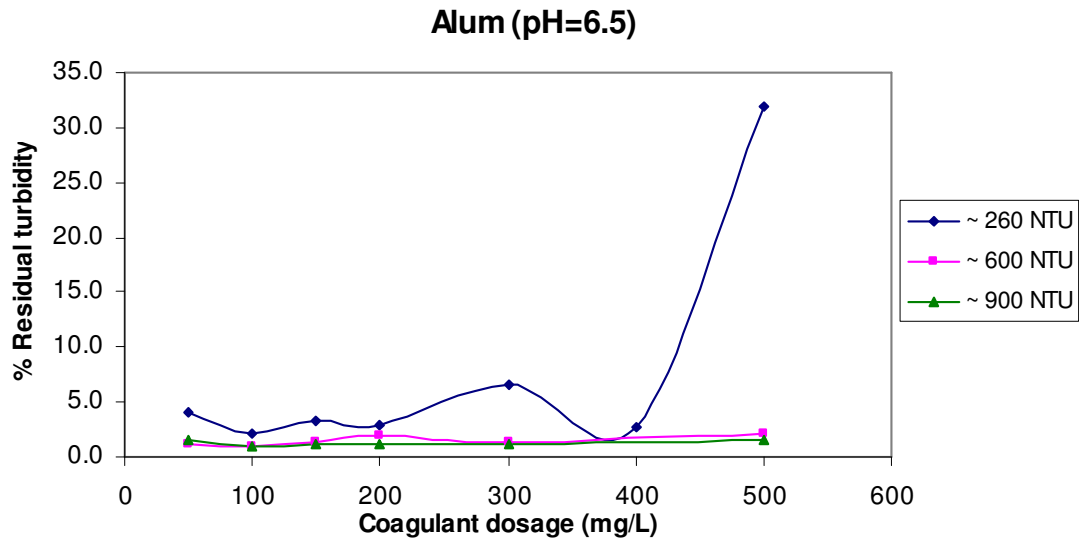


Fig. 5.4. Effect of aluminum sulfate dosage on the removal of turbidity at pH=6.5 and at different initial suspension turbidities

The lowest residual turbidity was established at 100 mg/L dosage at pH=6.5 and for all the initial suspension turbidities. This is observed in Fig.5.5.

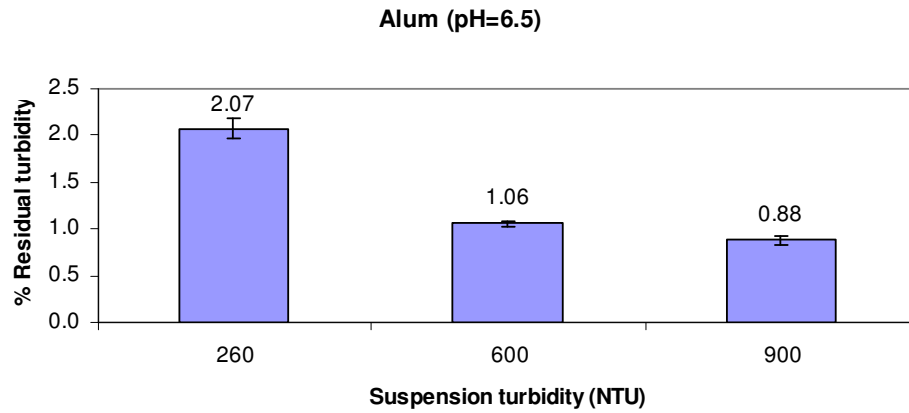


Fig. 5.5. Effect of initial suspension turbidity on its removal at pH=6.5 and 100 mg/L of alum

Since, 100 mg/L dosage and ~900 NTU were the optimal results for alum at pH=6.5 (with %R.T.= 0.88), these conditions were repeated at pH = 5.0 and pH=8.0 (Fig. 5.6).

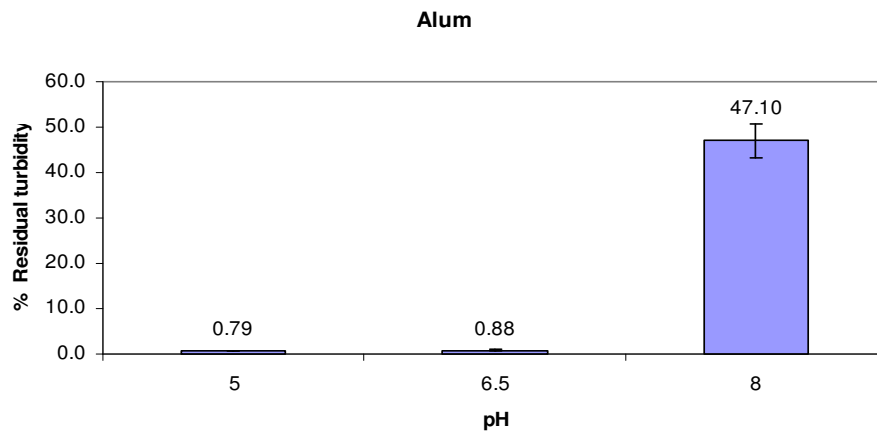


Fig. 5.6. Effect of pH on the removal of turbidity (100 mg/L of alum and initial suspension turbidity ~900 NTU)

Alum had some advantages such as ease of handling, was not hygroscopic and did not change the color of suspension. On the other hand, alum produced large volumes of sludge since about 100 mg/L is needed.

The more concentration of suspended solids expressed as initial suspension turbidity, the less residual turbidity at the same coagulant dosage (as shown in Fig. 5.4 and 5.5) due to the smaller distance among particulates. Low residual turbidity was reached at the lowest pH=5 because the soluble hydrolysis products were more insoluble at this low value, thus enhancing particle destabilization. In this case, it was speculated that alum was added in a sufficient amount that hydrolysis products exceeded the solubility of the metal hydroxide so that they were adsorbed onto particles and enmeshed the particles/precipitate. Furthermore, it was speculated that negatively charged species (like $\text{Al}(\text{OH})_4^-$) were present at this pH=5.0, thus led to effective destabilization of positively charged alumina particles. At pH values greater than 6.5 (above IEP for alumina CMP slurry) the predominant amorphous precipitate of aluminum and negatively charged alumina particles interacted due to their opposite charge and, thus caused aggregation. But sweep floc/charge neutralization was determinant at pH=5.0 to enmesh particles and promote removal. At the optimal operating conditions, the mechanism of colloid destabilization was brought about by a combination of adsorption/charge neutralization and mostly enmeshment (sweep floc). Final turbidity for optimal conditions was 7.2 NTU.

ii) Ferric sulfate

This inorganic coagulant was not as effective as alum and the optimal conditions were established at pH=5.0, 50 mg/L dosage, initial suspension turbidity of approximately 600 NTU and with % R.T. = 1.57 %.

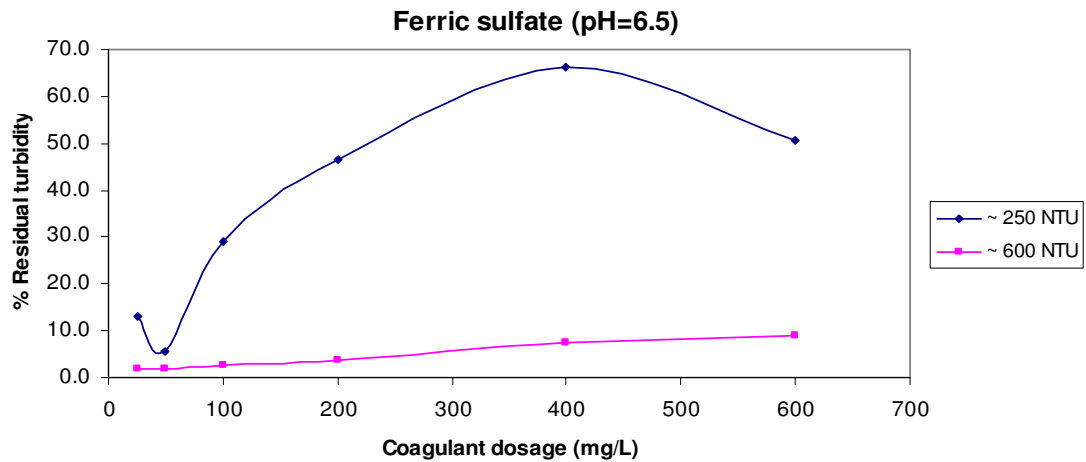


Fig. 5.7. Effect of ferric sulfate dosage on the removal of turbidity at pH=6.5 and at different initial suspension turbidities

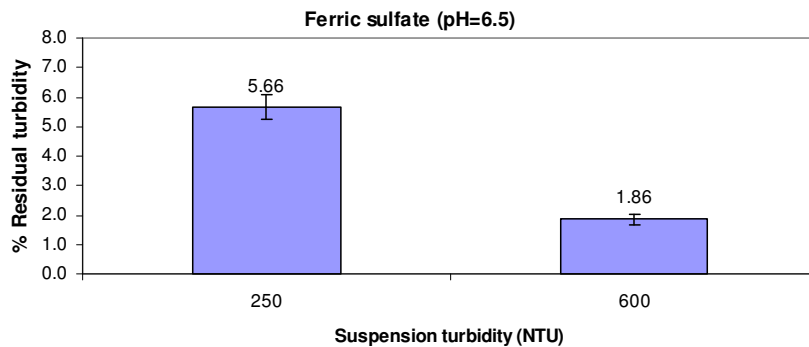


Fig. 5.8. Effect of initial suspension turbidity on its removal at pH=6.5 and 50 mg/L of ferric sulfate

The results for ferric sulfate are depicted in Fig. 5.7 to 5.9. The lowest residual turbidity was established at 50 mg/L dosage for pH=6.5 and for both initial suspension turbidities. Then, 50 mg/L and ~600 NTU were stated as the optimal conditions and later was evaluated at pH=5.0 and pH=8.0 in order to search for the best pH of coagulation.

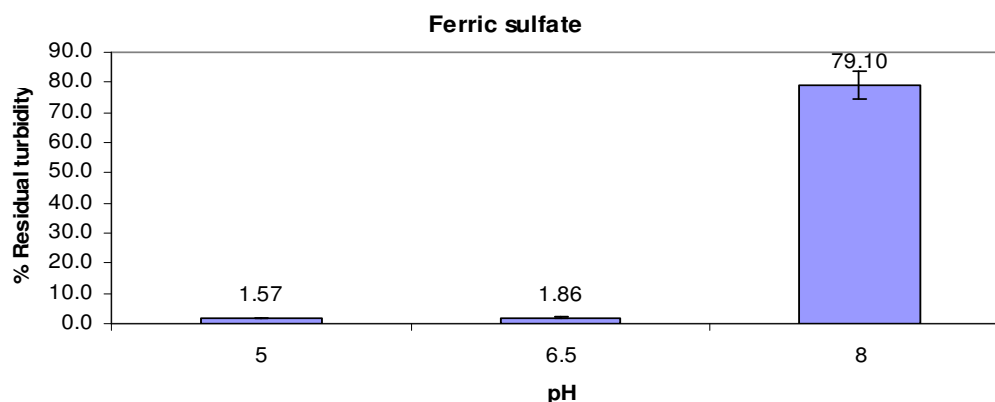


Fig. 5.9. Effect of pH on the removal of turbidity (50 mg/L of ferric sulfate and initial suspension turbidity ~600 NTU)

Therefore, pH=5.0 was found to be the best condition to destabilize alumina nanoparticles.

Ferric sulfate had a good removal of solids with a lower coagulant dosage as compared to alum. On the other hand, it was difficult to handle and humidified rapidly (hygroscopic), and this coagulant changed the color of suspension to yellowish which indicated a poor quality of the treated wastewater.

Since it was an inorganic coagulant and at optimum pH was 5.0, it was speculated that the mechanism of destabilization was brought about by adsorption and mostly enmeshment.

Above pH=4.0 for ferric ion, the formation of an amorphous precipitate occurred rapidly, causing entrapment of the particulates. That ‘sweep floc’ mechanism required a greater quantity of coagulant which was achieved with 50 mg/L of ferric sulfate. At the same time, the hydrolysis products were most insoluble at lower pH so that was another reason why the lowest residual turbidity was reached at pH=5.0. Final turbidity of the sample for optimal conditions was 8.8 NTU.

iii) Chitosan

For chitosan, a natural cationic coagulant, it was observed that the optimal conditions were at pH=7.0, 1.6 mg/L dosage and initial suspension turbidity of approximately 200 NTU with % R.T. = 0.30 %.

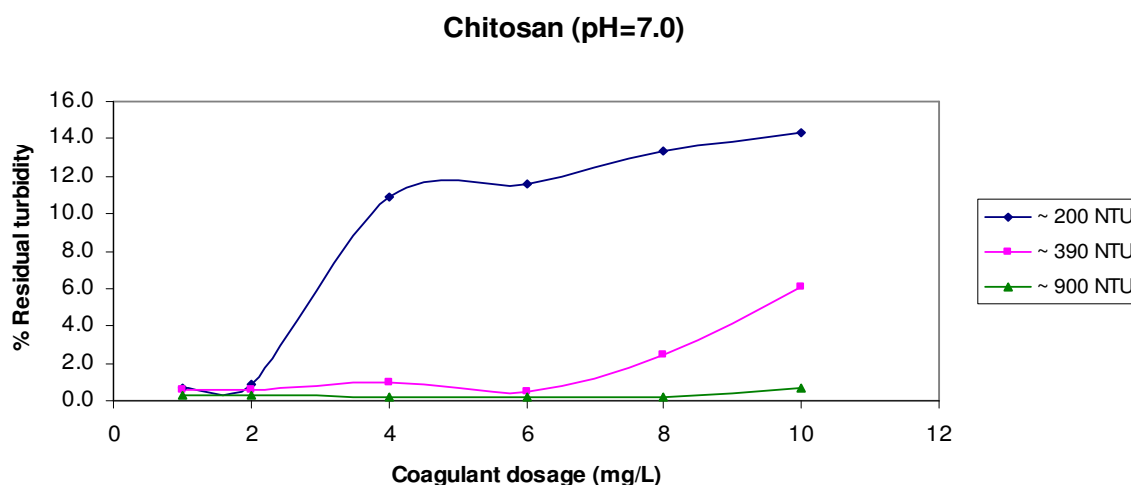


Fig. 5.10. Effect of chitosan dosage on the removal of turbidity at pH=7.0 and at different initial suspension turbidities

Experimental results at different initial suspension turbidities are well observed in Figs. 5.11 and 5.12. It is clearly observed from the figures that chitosan yields the lowest residual turbidity for the highest colloid concentration but with the highest chitosan dosage. That was due to the fact that the greater the presence of solids in suspension the more chemical coagulant was needed to destabilize the system and then particles were well removed due to the small distance between particles so that they could be enmeshed and swept out.

Basically what was looked for was the smaller coagulant use with a satisfactory level of solids removal, and for that reason 1.6 mg/L dosage of chitosan was chosen as the optimal dosage with a residual turbidity of 0.30%.

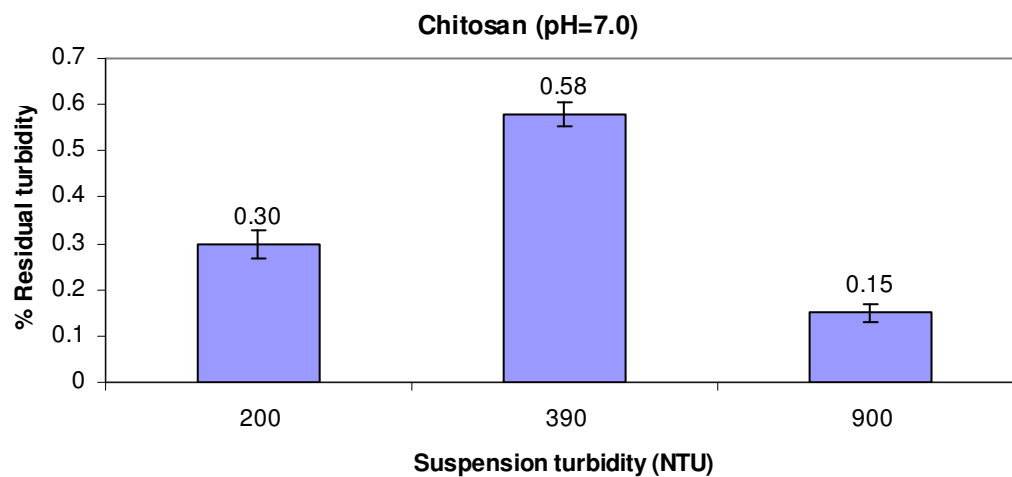


Fig. 5.11. Effect of initial suspension turbidity on its removal at pH=7.0

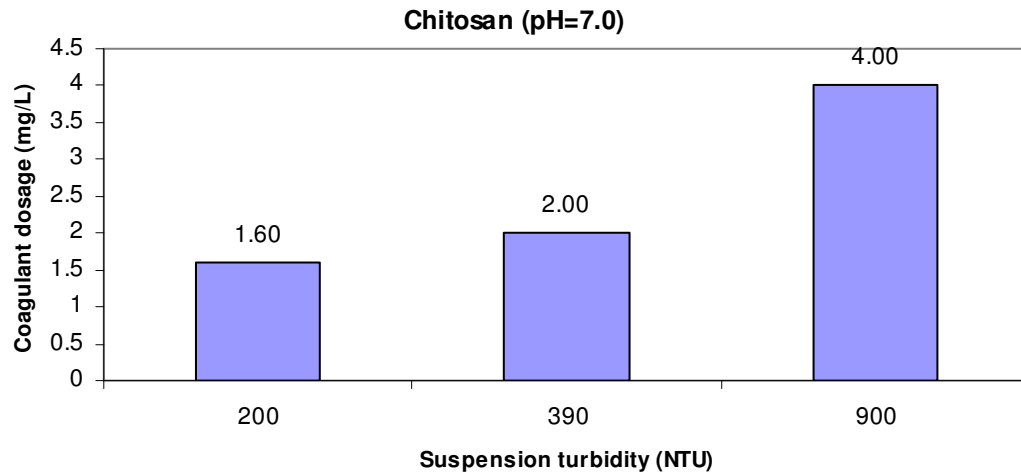


Fig. 5.12. Effect of initial suspension turbidity on the coagulant dosage (pH=7.0)

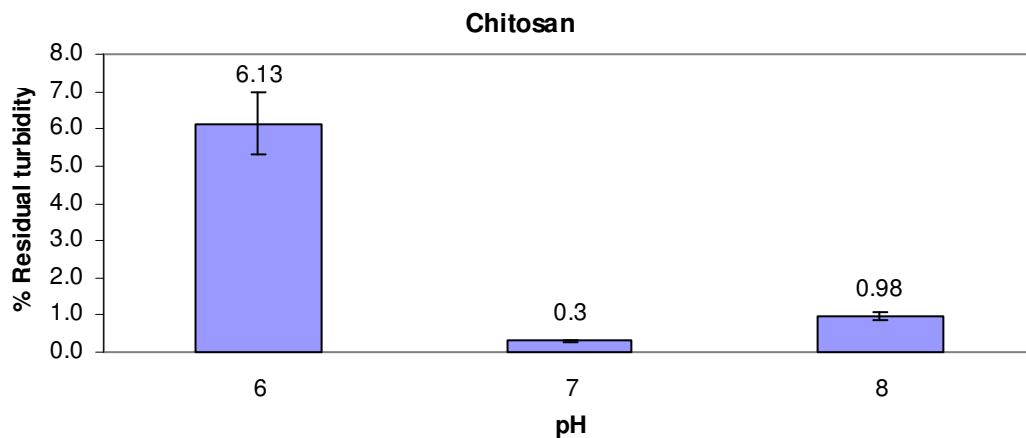


Fig. 5.13. Effect of pH on the removal of turbidity (1.6 mg/L of chitosan and initial suspension turbidity ~200 NTU)

The optimum pH of coagulation for chitosan was found to be 7.0 and a % R.T. of 0.3%.

Chitosan had many advantages such as excellent removal of solids with small coagulant dosages within an acceptable time of sedimentation and it did not change the color of suspension and sludge. At the same time the drawbacks were its virtual insolubility in water

if pH is above 6.5 so it had to be dissolved in 1% acetic acid solution, and the high cost of this coagulant.

Optimal dosage was dissimilar for each level of dilution due to a direct relationship between coagulant dose and concentration of particles. Since chitosan was a cationic natural polymer and optimum pH determined to be 7.0, it had considerable capability for coagulation/flocculation of negative colloidal systems such as alumina particles present in CMP waste samples (noting that above 6.5, alumina is negatively charged). Optimal pH of coagulation was 7.0 and it was due to the fact that it was close to the isoelectric point (IEP~6.5 as observed in the literature) of this slurry where repulsive forces between the particles were small, allowed the particles to approach each other and to eventually agglomerate. It was speculated that destabilization of the colloidal suspension was achieved by adsorption/charge neutralization and interparticle bridging. It was an effective coagulant that increased size and weight of flocs thus settled down rapidly. Final turbidity of the sample for optimal conditions was 1.8 NTU.

iv) Polyacrylamide

Polyacrylamide, a nonionic synthetic polymer, did not acquire ionic charge. Optimal operating conditions were not as much effective as chitosan and were established at: pH=7.0, 315 mg/L dosage and initial suspension turbidity of ~ 190 NTU with % R.T. = 4.71%.

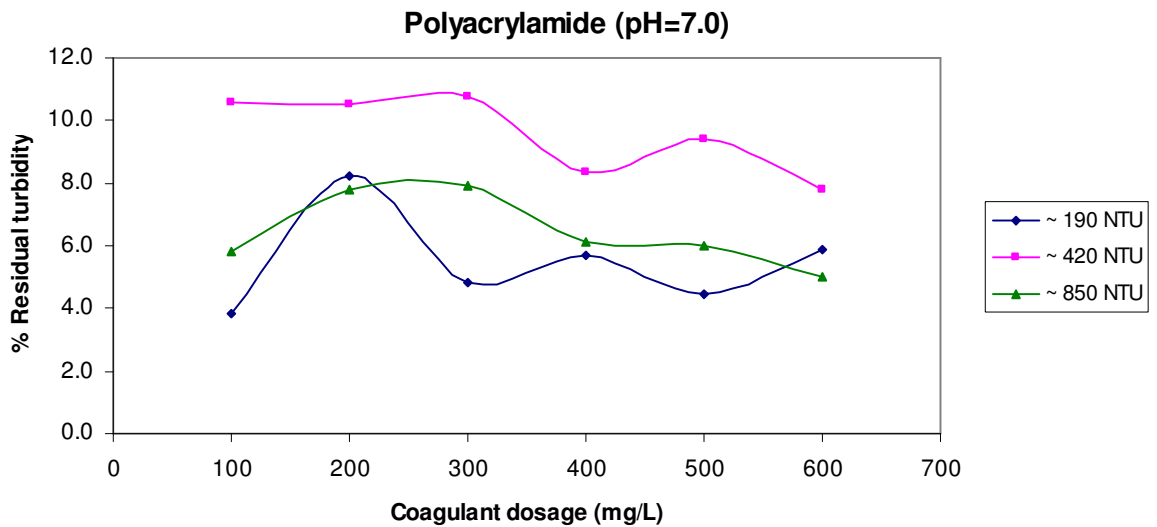


Fig. 5.14. Effect of polyacrylamide dosage on the removal of turbidity at pH=7.0 and at different initial suspension turbidities

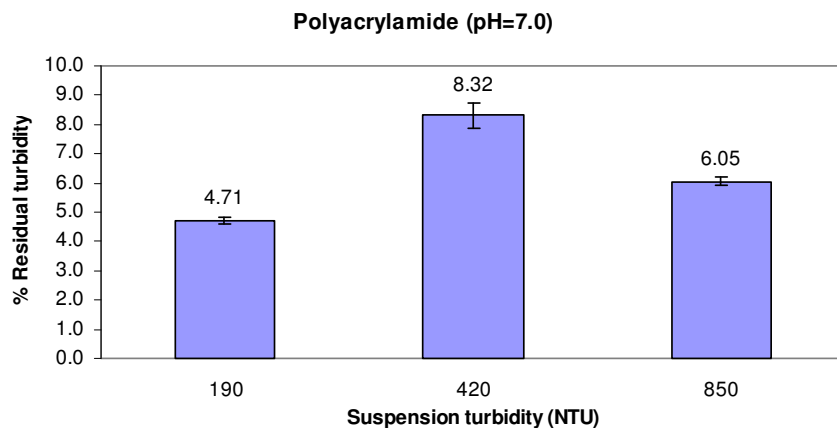


Fig. 5.15. Effect of initial suspension turbidity on its removal at pH=7.0

It is clearly observed in Fig. 5.15 that at the lowest suspension turbidity the lowest residual turbidity was attained. Hence, 315 mg/L dosage and approximately 190 NTU as initial suspension turbidity produced the best results and, later samples were evaluated at pH=6.0 and pH=8.0.

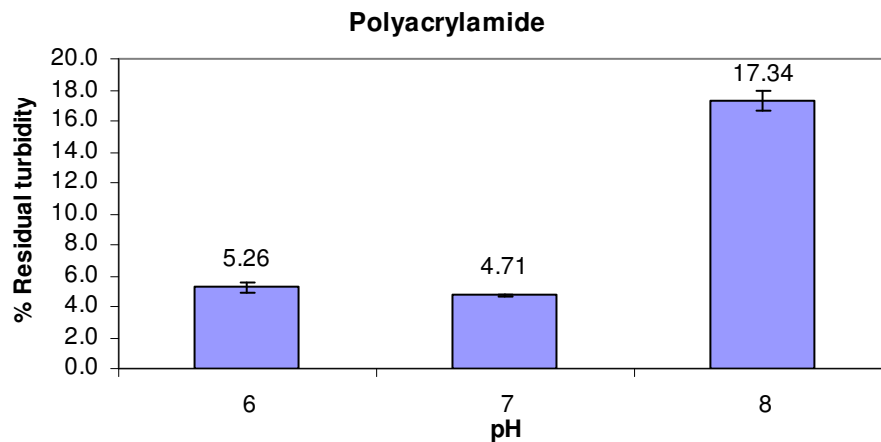


Fig. 5.16. Effect of pH on the removal of turbidity (315 mg/L of polyacrylamide and initial suspension turbidity ~190 NTU)

Therefore, pH=7.0 was the best pH of coagulation for polyacrylamide.

An advantage of this coagulant was that it led to a small amount for coagulation. On the other hand, polyacrylamide had a high viscosity thus was difficult to handle and also was an expensive coagulant. There was neither valuable removal of solids nor satisfactory time of sedimentation.

It was thought that since polyacrylamide has a high molecular weight and no ionizable groups, it was not able to effectively destabilize charged particles in CMP slurry. Coagulation would be enhanced, using polyacrylamide as a flocculant aid in conjunction

with alum or ferric sulfate. At high pH values, alumina particles acquired negative charges thus increasing the repulsive forces among them and hindered aggregation. Destabilization was brought about by enmeshment and interparticle bridging. Final turbidity of the sample for optimal conditions was 8.5 NTU.

v) Anionic polymer

Last but not least, an anionic polymer was utilized to remove particles in CMP waste samples. The optimal conditions were: pH=7.0, 75 mg/L dosage and initial suspension turbidity of approximately 190 NTU with %R.T. of 0.20 %.

This type of anionic polymer had a particular behavior with negatively charged alumina particles at the optimal pH=7.0 as it is shown in Figures 5.17, 5.18, 5.19 and 5.20.

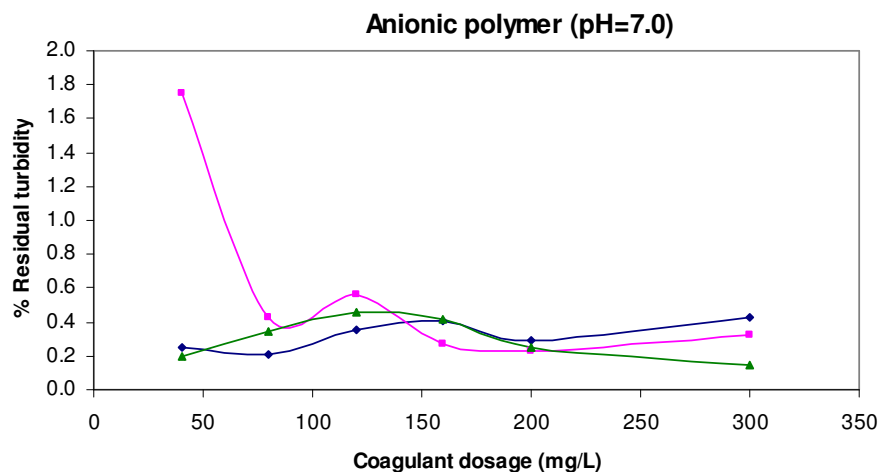


Fig. 5.17. Effect of anionic polymer dosage on the removal of turbidity at pH=7.0 and at different initial suspension turbidities

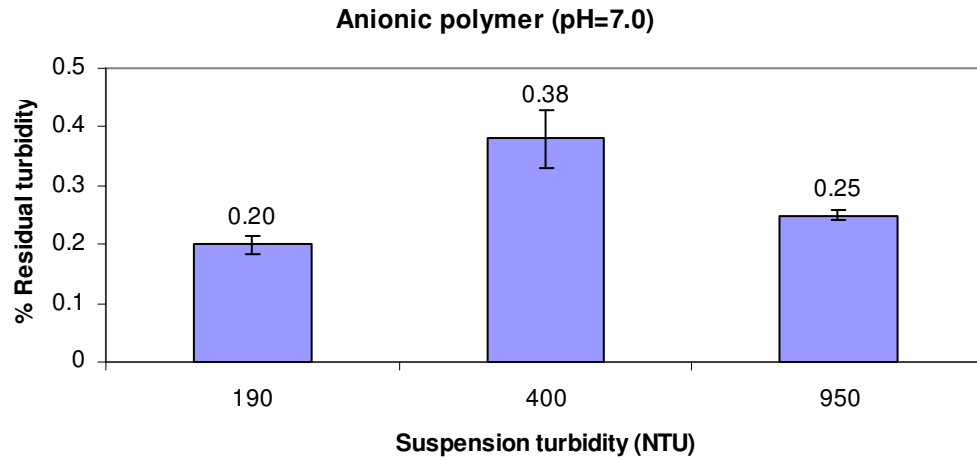


Fig. 5.18. Effect of initial suspension turbidity on its removal at pH=7.0

Anionic polymer left a residual turbidity of 0.20% at the optimal conditions of 75 mg/L dosage and approximately 190 NTU at pH=7.0. Then, these conditions were repeated at distinct pH values of 6.0 and 8.0.

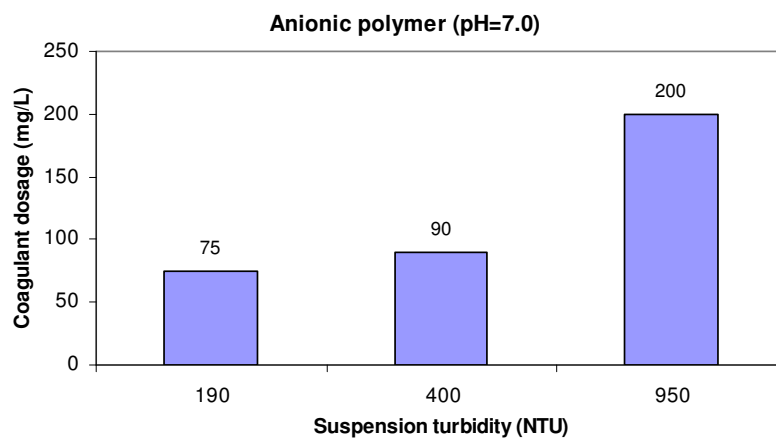


Fig. 5.19. Effect of initial suspension turbidity on the coagulant dosage (pH=7.0)

In Fig. 5.19, the more the suspension turbidity or colloid concentration the more the coagulant required, owing to the great amount of solids in suspension. The best pH of coagulation was pH=7.0 for the anionic polymer as shown in Fig. 5.20.

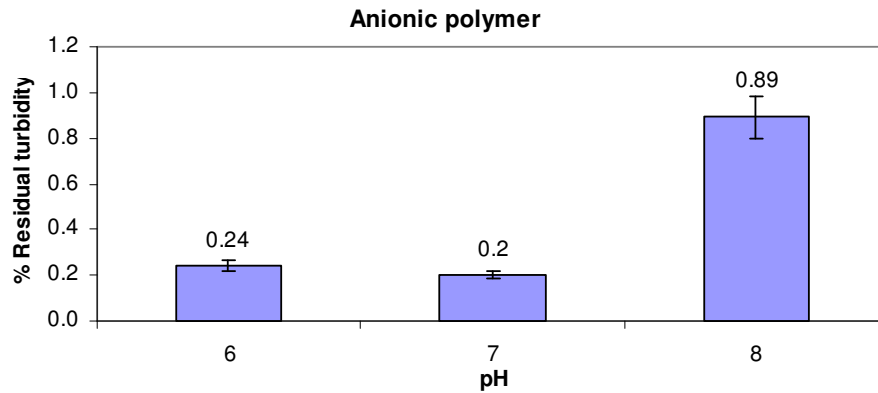


Fig. 5.20. Effect of pH on the removal of turbidity (75 mg/L of anionic polymer and initial suspension turbidity ~190 NTU)

Anionic polymer tended to swell, in this way particles were effectively removed and subsequently settled down in an acceptable time frame. Outstanding removal of turbidity and suspended solids was achieved and gave a clear supernatant solution. Some drawbacks can be enlisted such as its high cost (about \$2.00 per lb) and uncertainties regarding chemical impurities associated with this polymer, it was hygroscopic and difficult to handle.

In terms of residual turbidity, the anionic polymer gave the best results as compared to the other coagulants used in this research. Since this anionic polymer was not believed to destabilize the negatively charged particles, nevertheless it did and was suspected to be due to a phenomenon termed depletion flocculation (Asakura, 1954; Jenkins, 1996). During depletion flocculation, solvent tried to leave the gap between particles thus created an

osmotic pressure and pulled the two particles together (depletion attraction) as shown in Fig. 5.21. It was suspected that bridging brought the particles into contact so that they collided, stuck together and grew to a size that readily settled down. Therefore, the mechanism for destabilization was speculated to be a combination of interparticle bridging and depletion flocculation. It was observed that the highest pH the highest residual turbidity (Fig. 5.20) owing to the increased repulsive forces among negatively charged particles as pH augmented. In Fig. 5.19, the more the concentration of particles the more the negative charges present in the system, thus more coagulant dose was necessary. Final turbidity of the sample for optimal conditions was 0.40 NTU. Anionic polymer was also known to double as a flocculant in skimmers for sludge separation from treated water (Melendez, 2002).

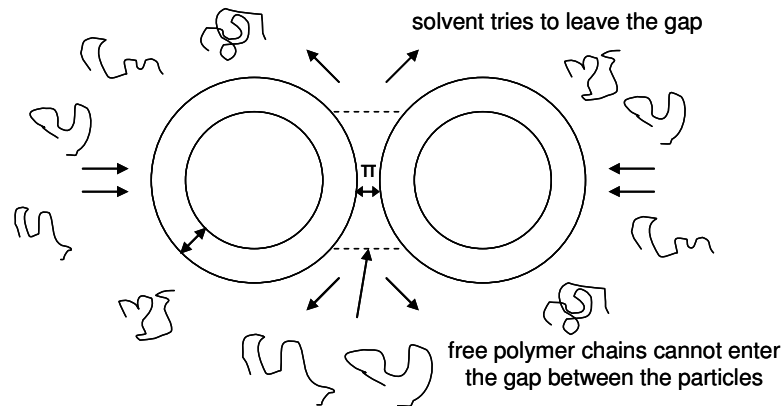


Fig. 5.21. Depletion flocculation between two particles in colloidal dispersion

The optimum operating conditions for each coagulant are listed in Table 5.2:

Table 5.2 Optimum operating conditions for coagulation process

Coagulant	Coagulant dosage (mg/L)	pH	Initial suspension turbidity (NTU)	Settling time (min)
Alum	100	5.0	900	18
Ferric sulfate	50	5.0	600	18
Chitosan	1.6	7.0	200	5
Polyacrylamide	315	7.0	190	25
Anionic polymer	75	7.0	190	2

5.3. Chemical coagulation and filtration experiments

During coagulation/flocculation process, nanoparticles were stuck together and formed flocs of great size and volume, and subsequently were separated by means of filtration. In this procedure, agglomerates present in the CMP waste after coagulation were removed from the liquid by means of a porous medium which retained the particulate matter but allowed the liquid to pass. It was reported (Stanley & Ogden, 2003) that the nanoparticles in CMP slurries were about 200-nm size. The objective of coagulation is to increase the particle size to enable use of high-efficiency filters on the market for removing the aggregated particles.

It was necessary to compare the results obtained by means of coagulation followed by gravity settling (section 5.2) with the results obtained via filtration.

Experiments were performed with three filters with different pore sizes:

- Filter paper Whatman # 2 Qualitative (8 μm)
- Filter paper Whatman # 50 Hardened (2.7 μm)
- Corning 430049 bottle top sterile filter (0.2 μm , nylon)

Chemical coagulants used for filtration experiments were the same ones that were used in coagulation experiments such as alum, ferric sulfate, chitosan, polyacrylamide and anionic polymer. It is important to highlight that these experiments were conducted at the optimal operating conditions obtained in section 5.2.

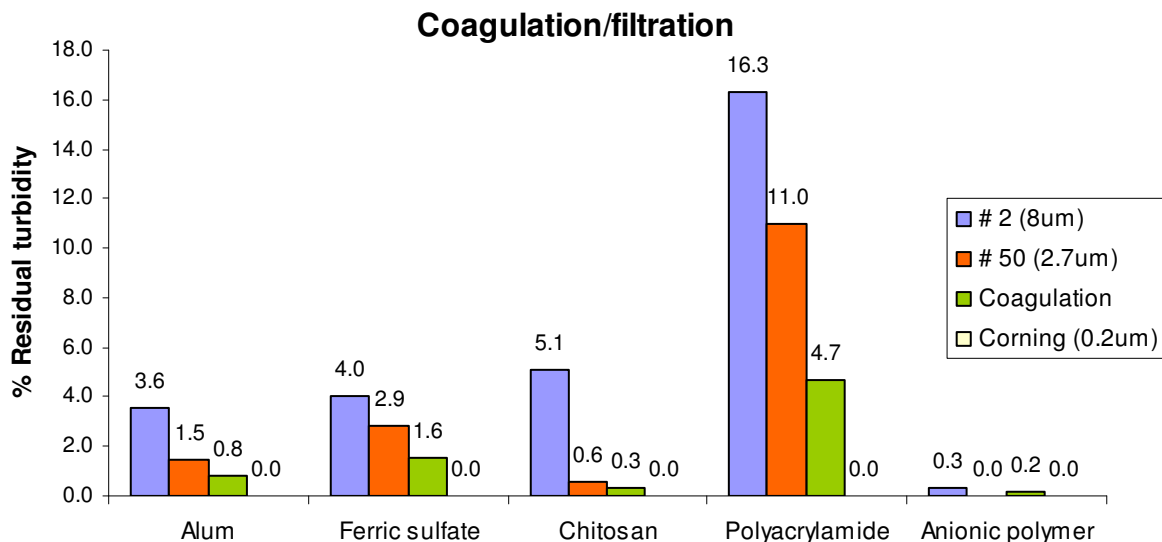


Fig. 5.22. Effect of coagulants on the removal of turbidity using filters with different pore sizes and a comparison with coagulation

Coagulation followed by filtration had as purpose to improve the removal of large size flocs. For filters with pore sizes of 8 μm and 2.7 μm its removal was not as effective as compared with coagulation followed by sedimentation (section 5.2). Nevertheless, when Corning filter (0.2 μm) was utilized, it indeed removed 100% of the flocs and a solution with no turbidity was obtained. In this manner, the agglomerated particles (flocs) that all coagulants formed had particle sizes greater than 0.2 μm . In the case of anionic polymer, their flocs were even greater than 2.7 μm and for chitosan the great majority of particles possessed sizes greater than 2.7 μm . For the rest of the coagulants, their flocs had varying particle sizes but bigger than 0.2 μm as mentioned.

Therefore, suitable results were obtained by means of coagulation in conjunction with filtration using Corning filter. Final turbidity of all the filtrated samples was 0.0 NTU, thus complied with regulations regarding treated wastewater.

5.4. Chemical coagulation of copper CMP samples

Chemical mechanical planarization is a process that disposes of alumino silicate nano-sized particles and a significant amount of copper ions which form a high pollutant wastewater whose contaminants should be removed by means of novel methods of solid removal.

Chemical coagulants used for experiments with copper CMP waste samples were the ones that effectively removed solids in section 5.2 such as alum, chitosan and anionic polymer.

Two types of copper CMP waste samples were used:

- Cu-CMP waste obtained from the University of Arizona tool room
- Cu-CMP waste prepared from commercial CMP slurry and a 1000 ppm copper solution.

To simulate the slurry waste obtained from copper CMP process, three distinct concentrations of copper (II) (25, 50 and 100 ppm) were prepared from alumina-commercial CMP slurry with the purpose of comparing their performance and their affinity to be destabilized with the addition of aforementioned chemical coagulants.

Copper ions distributed between liquid phase and nanoparticles in compounds such as copper ions, oxides, hydroxides, complexes, adsorbed or absorbed species. In addition they competed with other chemicals present in CMP slurry or hydrolysis products formed during coagulation of inorganic coagulants.

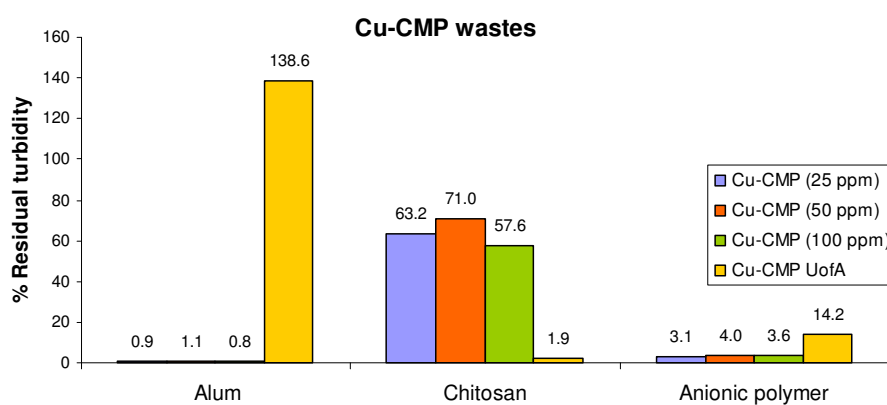


Fig. 5.23.Effect of coagulants on the removal of turbidity with different Cu-CMP wastes (alum at pH=5.0, 100 mg/L; chitosan at pH=7.0, 1.6 mg/L; anionic at pH=7.0, 75 mg/L)

CMP process involved complex interactions between the slurry and the metal during polishing which made difficult to understand the behavior of the colloidal suspension.

For that reason, it was relevant to visualize the complex interactions between coagulant-copper-nanoparticles in order to comprehend the possible mechanisms influencing separation.

Both Cu-CMP waste samples were composed of chemical additives such as abrasives (alumina or silica), surfactants, inhibitors, complexing agents, oxidizers (H_2O_2) whose solubility was pH dependent (Ihnfeldt & Talbot, 2006).

Alum showed a good performance with Cu-CMP prepared from commercial CMP slurry. At low pH, copper and its transition complexes were highly soluble with some of the copper particles dissolving to Cu^{2+} while the repulsive forces between the positively charged alumina particles and these ions decreased its agglomeration. Hence, the addition of aluminum sulfate and instantaneous formation of hydrolysis products interacted with both compounds, and by means of enmeshment (sweep floc) turbidity was finally diminished. On the other hand, Cu-CMP from the University of Arizona tool room showed an increase of the turbidity owing to the restabilization of the colloidal system and was due to that aluminum hydroxide, an insoluble precipitate formed during hydrolysis of alum, competed with complexants and sequestered transition metal ions by adsorption and absorption processes thus remained in solution and decreased the efficiency of solids removal.

Chitosan exhibited a behavior different from alum, producing a low residual turbidity with the second copper-based sample. At a pH=7.0, copper in water oxidized to either cupric oxide (CuO) or cuprous oxide (Cu_2O) which were positively charged (Ihnfeldt & Talbot,

2006), whereas silica acquires a negative charge. Therefore, these oppositely charged CuO and silica caused an increase in the agglomeration so that chitosan trapped these flocs and swept and engulfed them thus forming large volume precipitates that easily settled down. In the case of the first sample, chitosan, copper oxides, alumina and all unknown compounds interacted in an uncertain and complex way so that influenced the removal.

Anionic polymer along with the first sample left an approximate residual turbidity of 3.5%, while with the second sample it was about 14%. That difference may be to the presence of unidentified chemical components which did not permit depletion flocculation to occur thus separated particles and avoided them to be engulfed and precipitated as it was expected. Even though, residual turbidity was 14%, final turbidity was 3.5 NTU which was an adequate value for the purpose of the present study.

5.5. Comparison of results

In order to determine the most effective coagulant to separate nano-sized alumina particles in CMP wastes, a comparison was made on basis of the percentage of residual turbidity and solids removal (as shown in Fig. 5.26).

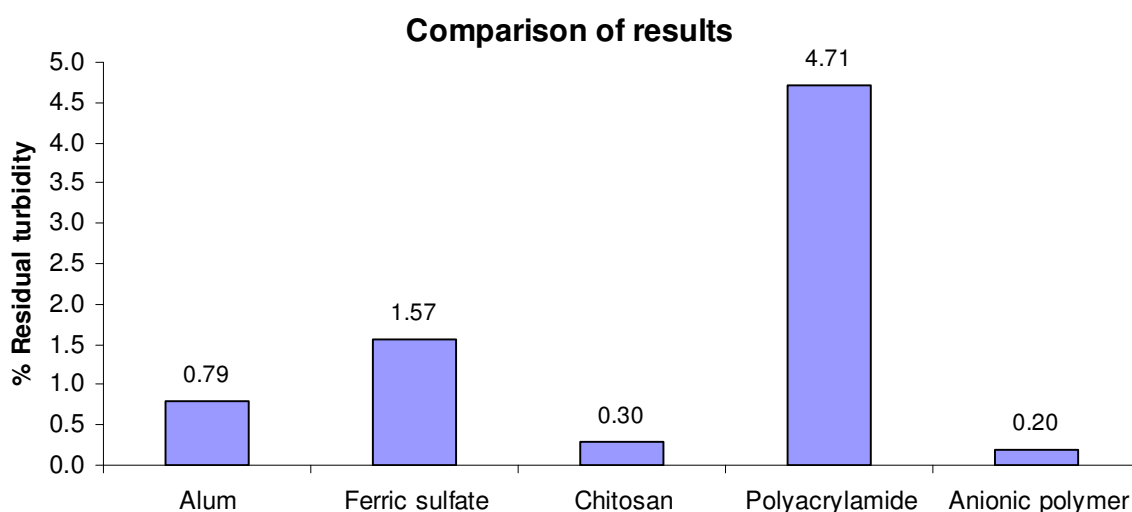


Fig. 5.24. Comparison of coagulants on the removal of turbidity by means of coagulation (commercial CMP slurry from Cabot Microelectronics iCue[®] 5001)

As it is shown in Fig. 5.22 (chemical coagulation followed by filtration) and Fig. 5.24 (chemical coagulation) either anionic polymer, chitosan and alum, in this order, demonstrated a low residual turbidity and a consequent reduction of nanoparticles in suspension.

Also, anionic polymer produced good results with copper-based CMP samples which confirmed its flexibility for distinct operating conditions, versatility and effectiveness to reduce the concentration of nanoparticles in CMP wastes.

Therefore, the anionic polymer was the best coagulant to remove copper and nanoparticles from CMP wastes.

Flocs formed during coagulation should settle rapidly and be resistant to destruction by shearing forces. Unfortunately, alum produced a light-weight, fragile, slow-settling floc (Fig. 5.25) consisting primarily of $\text{Al}(\text{OH})_3$. Hence, an additional experiment was carried out to improve floc properties and enhance coagulation using alum as primary coagulant (100 mg/L dosage, pH=5.0, initial turbidity ~900 NTU) and anionic polymer as coagulant aid (75 mg/L dosage and added during slow mixing step). That resulted in a residual turbidity of 0.17%, even better than coagulation with alum or anionic polymer alone, and a rapid settling (2 min).

Fig. 5.25 illustrates the short settling time for the anionic polymer which was due to the macroflocs formed during its coagulation which allowed a rapid sedimentation.

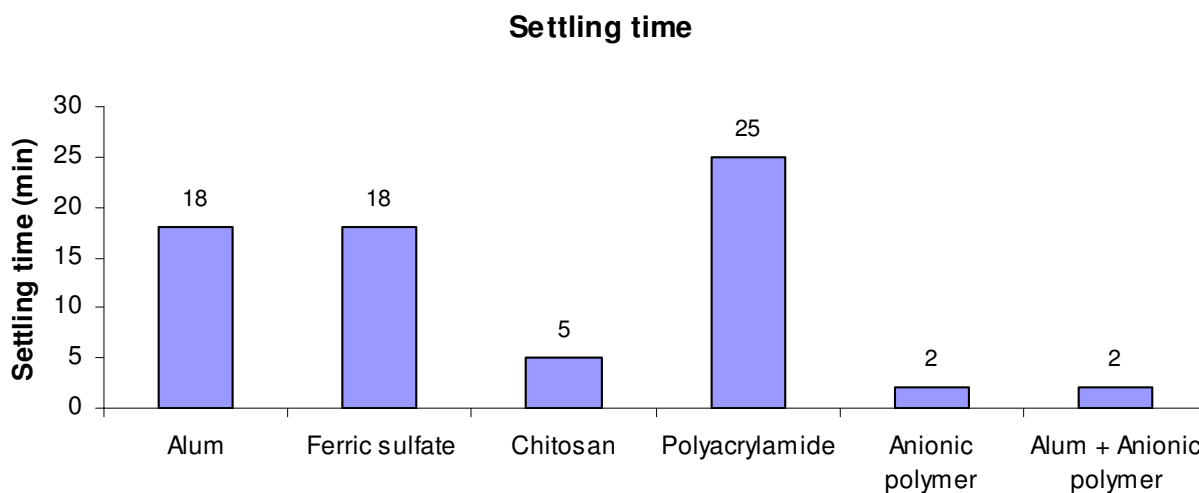


Fig. 5.25. Settling time for different coagulants at the optimal operating conditions using commercial CMP slurry

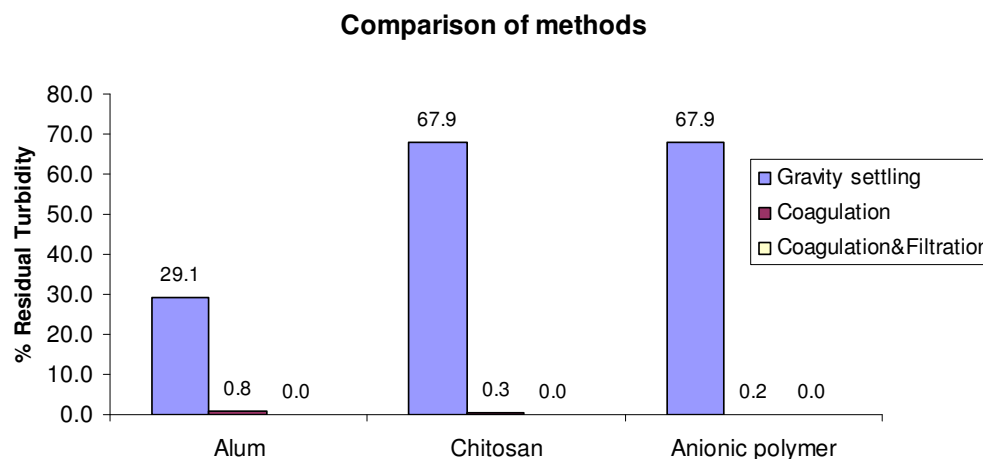


Fig. 5.26. Comparison of methods to remove nanoparticles using commercial CMP slurry with alum, chitosan and anionic polymer (initial suspension turbidity ~900 NTU, ~200 NTU and ~190 NTU)

Fig. 5.26 shows a great difference between separation by gravity settling compared to coagulation and coagulation/filtration. In this way, the efficiency was improved and justified this novel separation method.

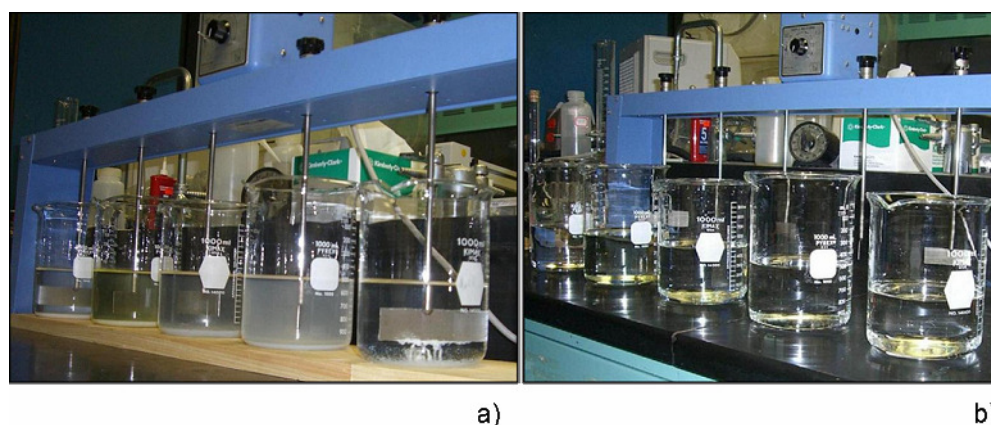


Fig. 5.27. Chemical coagulation followed by sedimentation (a) and followed by filtration (b). Left to right: alum, ferric sulfate, chitosan, polyacrylamide and anionic polymer

5.6. Chemical coagulation with other CMP slurries

Additionally, some experiments were conducted with other CMP waste samples such as silica CMP slurry and surrogate CMP waste. Because of the small volumes available, these CMP wastes were used in only a few experiments. Optimal operating conditions for coagulants were used (as shown in Table 5.2).

Coagulation process using alum, chitosan and anionic polymer did not give satisfactory results and turbidity was increased. Silica particles are negatively charged at $\text{pH} > 6.0$ and different interactions were present between coagulant-silica CMP slurry. Silica based-slurry demonstrated slow settling behavior as compared to alumina-based slurry, and that also contributed to an increase on the turbidity. Additional experiments should be conducted to determine the optimum operating conditions due to the fact that the ones found in section 5.2 only applied to alumina CMP slurry.

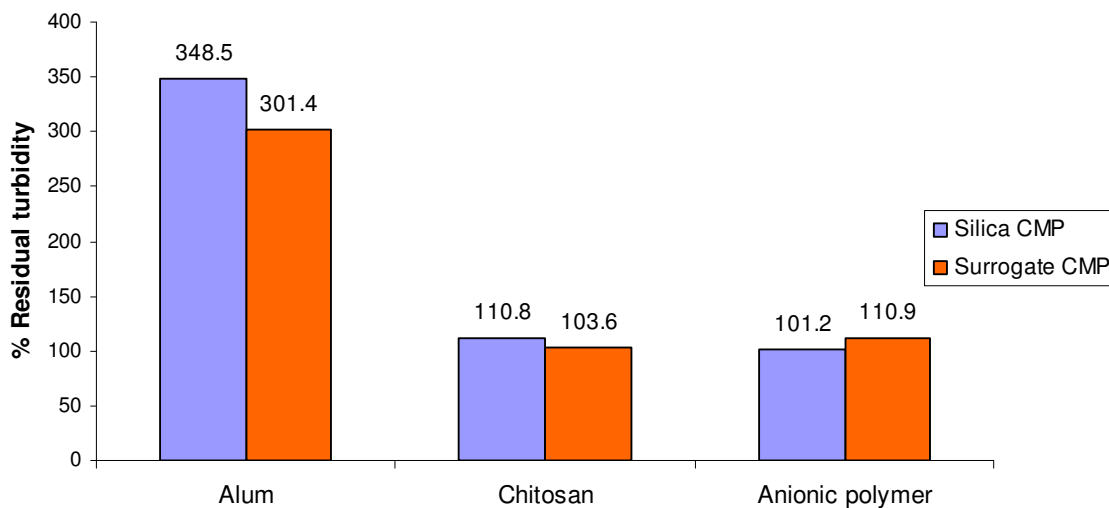


Fig. 5.28. Chemical coagulation with silica-based CMP slurry and surrogate CMP waste

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

Coagulation of chemical mechanical planarization wastes was studied. This chemical treatment method was used to remove mainly copper and alumina nanoparticles present in some copper CMP waste samples. Subsequently, since about forty-five percent of the copper ions adhere to the particles, coagulation also removed half of the copper from the waste.

Based on the experimental results, the following conclusions can be drawn:

- 1) Commercially available alumina-based CMP slurry was characterized and evaluated in order to establish the optimal operating conditions for removing particulates by means of chemical coagulation followed by sedimentation and by filtration. It was found that the original raw slurry had a high total solids content (54480 mg/L) and high turbidity (greater than 13500 NTU) and when it was diluted these values were reduced to within a range of 600-2400 mg/L and 100-1000 NTU, respectively.
- 2) Five chemical coagulants were evaluated to treat alumina-based CMP slurry (Cabot Microelectronics iCue[®] 5001) and the following parameters were determined: pH, coagulant dosage and initial suspension turbidity (as shown in Table 6.1).

Table 6.1. Optimum parameters to remove nanoparticles in commercial CMP slurry

Coagulant	Coagulant dosage (mg/L)	pH	Initial suspension turbidity (NTU)	Settling time (min)
Alum	100	5.0	900	18
Ferric sulfate	50	5.0	600	18
Chitosan	1.6	7.0	200	5
Polyacrylamide	315	7.0	190	25
Anionic polymer	75	7.0	190	2

- 3) Comparisons to determine the most effective coagulant were made on basis of the residual turbidity, expressed as percentage of residual turbidity, and settling time. Residual turbidity was used to indicate the relative amount of particles remaining in treated CMP waste. Based on the results it was found that the anionic polymer was the most efficient at removing alumina particles and was also versatile to treat other CMP samples. Its mechanism to destabilize the colloidal system was recognized as depletion flocculation.
- 4) Over 95% turbidity reduction was achieved and less than 5 NTU (the recommended value for good quality water) was realized.
- 5) Removal of copper was evaluated qualitatively and by means of turbidity reduction. Since there was removal of turbidity, insoluble copper-based compounds and adsorbed copper were removed from CMP waste. Copper was suitably removed by the anionic polymer.

- 6) Chemical coagulation was found to be very effective and viable to reduce the amount of nanoparticles and copper in CMP wastes. In this way, the efficiency of the subsequent biotreatment can be improved.

6.2. Recommendations

Future work in this area should tend towards the characterization and evaluation of copper CMP wastes. The same optimal parameters should be determined as were done in the present study.

A quantitative investigation should be done in order to determine how much copper distributes between liquid phase and nanoparticles (before and after coagulation). In this way, a better understanding of interactions phenomenon can be visualized.

It is also recommended to conduct cross-flow filtration experiments. Furthermore, a method should be devised to dispose of the sludge containing copper either via encapsulation or sequestration.

APPENDIX A: EPA Method 160.3 Residue, Total

Method 160.3: Residue, Total (Gravimetric, Dried at 103-105°C)

Instrumentation: Drying Oven

2. Scope and Application

1.1. This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2. The practical range of the determination is from 10 mg/L to 20,000 mg/L.

2. Summary of Method

2.1. A well mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C.

3. Definitions

3.1. Total Residue is defined as the sum of the homogeneous suspended and dissolved materials in a sample

4. Apparatus

4.1. Evaporating dishes, porcelain, 90 mm, and 100 mL capacity. (Vycor or platinum dishes may be substituted and smaller size dishes may be used if required).

5. Procedure

- 5.1. Heat the clean evaporating dish to 103-105°C for one hour, if Volatile Residue is to be measured, heat at 550 ±50°C for one hour in a muffle furnace. Cool, desiccate, weigh and store in desiccator until ready for use.
- 5.2. Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven.
- 5.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.
- 5.2.2 If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and splattering of the sample.
- 5.3. Dry the evaporated sample for at least 1 hour at 103-105°C. Cool in a desiccator and weigh. Repeat the cycle of drying at 103-105°C, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5 mg, whichever is less.

6. Calculation

- 6.1. Calculate total residue as follows:

$$\text{Total residue, mg / L} = \frac{(A - B) \times 1000}{C}$$

Where:

A = weight of sample, + dish in mg

B = weight of dish in mg

C = volume of sample in mL

APPENDIX B: EPA Method 180.1 Turbidity

Method 180.1: Turbidity (Nephelometric)

Instrumentation: Turbidimeter

1. Scope and application

- 1.1. This method is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU). Higher values may be obtained with dilution of the sample.

Note: NTU's are considered comparable to the previously reported Formazin Turbidity Units (FTU) and Jackson Turbidity Units (JTU).

2. Summary of method

- 2.1. The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTU's, are made in a nephelometer designed according to specifications outlined in Apparatus. A standard suspension of Formazin, prepared under closely defined conditions, is used to calibrate the instrument.

- 2.1.1. Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.

- 2.1.2. A commercially available standard is also approved for use for the National Interim Primary Drinking Water Regulations. This standard is identified as AMCO-AEPA-1 available from Amco Standard International, Inc.

3. Interferences

- 3.1. The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner.
- 3.2. The presence of true color, that is the color of water which is due to dissolved substances which absorb light, will cause turbidities to be low, although this effect is generally not significant with finished waters.

4. Apparatus

- 4.1. The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photo-electric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period.
- 4.2. The sensitivity of the instrument should permit detection of a turbidity difference of 0.02 units or less in waters having turbidities less than 1 unit. The instrument should measure from 0 to 40 units of turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.
- 4.3. The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all

where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled.

4.4. Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension issued for calibration. To minimize such differences, the following design criteria should be observed:

4.4.1. Light source: Tungsten lamp operated at a color temperature between 2200-3000 °K.

4.4.2. Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

4.4.3. Detector: Centered at 90° to the incident light path and not to exceed $\pm 30^\circ\text{C}$ from 90°C. The Detector, and filter system if used, shall have a spectral peak response between 400 and 600 nm.

4.5. The Hach Turbidimeter, Model 2100 and 2100 A, is in wide use and has been found to be reliable; however, other instruments meeting the above design criteria are acceptable.

5. Reagents

5.1. Turbidity-free water: Pass distilled water through a 0.45F pore size membrane filter if such filtered water shows a lower turbidity than the distilled water.

5.2. Stock formazin turbidity suspension: Solution 1: Dissolve 1.00 g hydrazine sulfate, $(\text{NH}_2)_2\text{H}_2\text{SO}_4$, in distilled water and dilute to 100 mL in a volumetric flask. Solution 2: Dissolve 10.00 g hexamethylene-tetramine in distilled water and dilute to 100 mL in a volumetric flask. In a 100 mL volumetric flask, mix 5.0 mL Solution

1 with 5.0 mL Solution 2. Allow to stand 24 hours at $25 \pm 3^{\circ}\text{C}$, then dilute to the mark and mix.

5.3. Standard formazin turbidity suspension: Dilute 10.00 mL stock turbidity suspension to 100 mL with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity-free water as required.

5.3.1. A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

5.4. The AMCO-AEPA-1 standard as supplied requires no preparation or dilution prior to use.

6. Procedure

6.1. Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities. Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

6.2. Turbidities less than 40 units: Shake the sample to thoroughly sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

6.3. Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

6.3.1. The Hach Turbidimeters, Models 2100 and 2100A, are equipped with 5 separate scales: 0-0.2, 0-1.0, 0-100, and 0-1000 NTU. The upper scales are to be used only as indicators of required dilution volumes to reduce readings to less than 40 NTU.

NOTE 2: Comparative work performed in the MDQAR Laboratory indicates a progressive error on sample turbidities in excess of 40 units.

7. Calculation

7.1. Multiply sample readings by appropriate dilution to obtain final reading.

7.2. Report results as follows:

NTU	Record to nearest
0.0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

APPENDIX C: Dissolution of chitosan

Since chitosan is virtually insoluble in water under normal conditions, it is necessary to dissolve it in acidic medium. Usually 1 percent solutions of chitosan are prepared in 1 percent acetic acid. Other organic acids that can be substituted for acetic acid are adipic, formic, malic, propionic, or succinic acids. Formic acid has proved to be a good solvent over the entire acid concentration range from 0.5 to 50 percent.

To make a 1 percent solution in the laboratory:

- Disperse 2 g (dry basis) of chitosan in 100 mL of deionized water.
- Add 100 mL of 2 percent (2g/10mL) acetic acid with agitation at approximately 100 rpm for 60 min.

Note: Heating the solution accelerates the dissolving process, but it should not be as prolonged.

BIBLIOGRAPHY

- [1] Aksu S. and Doyle F. The role of glycine in the Chemical Mechanical Planarization of copper. *Journal of the Electrochemical Society*, 149 (6): G352-G361, 2002.
- [2] American Quality Water Works Association. *Water quality and treatment – A handbook of community water supplies*. Fifth edition, Chapter 6 by Letterman R., Amirtharajah A., O'Melia C., Mc Graw Hill, 1999.
- [3] American Water Works Association and American Society of Civil Engineers. *Water Treatment Plant Design*. Third edition, Mc Graw Hill Professional, 1997.
- [4] Asakura S. and Oosawa F. On interaction between two bodies immersed in a solution of macromolecules. *Journal of Chemical Physics*, volume 22 (7): 1255-1256, 1954.
- [5] Belongia B., Haworth P., Baygents J. and Raghavan S. Treatment of alumina and silica chemical mechanical polishing waste by electrodecantation and electrocoagulation. *Journal of the Electrochemical Society*, 146 (11) 4124-4130, 1999.
- [6] Benefield L., Judkins J., and Weand B. *Process Chemistry for Water and Wastewater Treatment*. Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1982.
- [7] Bogere M. Mass transport in porous media. 1. Prediction of breakthrough characteristics, presented at the American Filtration Society Annual Technical Conference 95, Nashville, TN, April 24-26, 1995.
- [8] Bogere M. and Willis M. Analysis of diffusion and mass transfer phenomena in multiphase-multicomponent systems. Application to heterogeneous processes with interfacial effects, *Chem. Eng. Sci.*, 48, 6, 1019-1031, 1993.
- [9] Bogere M. and Willis M. Analysis and prediction of filter cake washing. *Advances in filtration and separation technology*. Vol. 6: New filtration and separation equipment, 561-565, 1992.

- [10] Bogere M. and Willis M. Prediction of washing contaminants from porous media. Paper presented at the AIChE National Meeting, Miami Fl., November 1992.
- [11] Chin C., *et al.* Removal of nanoparticles from CMP wastewater by magnetic seeding aggregation. *Chemosphere In Press* 63(10):1809-1813, 2006.
- [12] Conner J. Chemical fixation and solidification of hazardous wastes. Van Nostrand Reinhold, New York, 1990.
- [13] Corlett G. CMP water reduction and waste treatment overview. *Semiconductor Online*, March 17, 1999.
- [14] Courduvelis C. and Gallagher G. Selective removal of copper or nickel from complexing agents in aqueous solution. US Patent 4303704, 1981.
- [15] Davis M. and Cornwell D. Introduction to Environmental Engineering. Fourth edition, Mc Graw Hill International edition, 2007.
- [16] Den W. and Huang C. Electrocoagulation for removal of silica nano-particles from Chemical Mechanical Planarization wastewater. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 254: 81-89, 2005.
- [17] Gadd G. Accumulation of metals by microorganisms and algae. *Biotechnology – A comprehensive treatise* (H.J. Rehm, ed.). VCH Verlagsgesellschaft, Weinheim: 401–433, 1988.
- [18] González M. Upflow anaerobic sludge blanket treatment of Mayagüez tuna industry wastewater, M.S. Thesis, University of Puerto Rico, Mayagüez, PR, 1996.
- [19] Golden J., Small R., Pagan L., Shang C. and Ragavan S. Evaluating and treating CMP wastewater. *Semiconductor Int.*, <http://www.e-insite.net/semiconductor>, 2000.
- [20] Grassi M., Shi B. and Allen H. Partition of copper between dissolved and particulate phases using aluminum oxide as an aquatic model phase: effects of pH, solids and organic matter. *Journal Brazilian Chemical Society*, Vol. 11 (5): 516-524, 2000.

- [21] Hawari A. and Mulligan C. Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass. *Bioresource Technology* 97-4: 692-700, 2006.
- [22] Hickey R. and Smith G. *Biotechnology in industrial waste treatment and bioremediation*. CRC Press, Boca Raton, FL, 1996.
- [23] Hinchee R. and Reisinger H. A practical application of multiphase transport theory to ground water contamination problems. *Ground Water Mon. Review*, Volume 7 #1: 84-92, 1987.
- [24] Hwang S., Bailey S., Brooks M. and Schroeder P. Evaluation of chemical clarification polymers and methods for removal of dissolved metals from CDF effluent. *DOER Technical Notes Collection*, Vicksburg, MS, 2006.
- [25] Ihnfeldt R. and Talbot J. The effects of copper CMP slurry chemistry on the colloidal behavior of alumina abrasives. *Journal of the Electrochemical Society*, 153 (11): G948-G955, 2006.
- [26] Jenkins P. and Snowden M. Depletion flocculation in colloidal dispersions. *Advances in colloid and interface science*, 68: 57-96, 1996.
- [27] Judd S. and Hillis P. Optimization of combined coagulation and microfiltration for water treatment. *Water Research* 35(12), pp.2895-2904, 2001.
- [28] Kawamura S. Effectiveness of natural polyelectrolytes in water treatment. *Journal of the American Water Works Association*, 83 (10): 88-91, October 1991.
- [29] Krulik G., Kramasz K., Golden J., Small R., Shang C. and Ragan L. Copper CMP wastewater chemistry and treatment. *Ultrapure Water* 18 (10) 29-35, 2001.
- [30] Lai C. and Lin S. Electrocoagulation of Chemical Mechanical Polishing (CMP) wastewater from semiconductor fabrication. *Chemical Engineering Journal* 95: 205-211, 2003.

- [31] Lai C. and Lin S. Treatment of Chemical Mechanical Polishing wastewater by electrocoagulation: system performances and sludge settling characterization. *Chemosphere* 54: 235-242, 2004.
- [32] Lazaridis N., Peleka E., Karapantsios Th. and Matis K. Copper removal from effluents by various separation techniques. *Hydrometallurgy* 74 (1-2), 149-156, 2004.
- [33] Lin S. and Yang C. Chemical and physical treatments of chemical mechanical polishing wastewater from semiconductor fabrication. *Journal of hazardous materials* 108 (12): 103-109, 2004.
- [34] Lin Y., Huang C., Sanders P., and Marinucci A. Separation of nano-sized naturally occurring particles by cross-flow electro-filtration process. *Keystone Water Quality Manager*, 198-203, 2002.
- [35] Lipp P., Lee C., Fane A. and Fell C. A fundamental study of the ultrafiltration of oil-water emulsions. *Journal of Membrane Science*, 36: 161-177, 1984.
- [36] McAneny J. and Welty J. Considerations of R&D scale CMP processing and its use in novel applications. EuroAsia semiconductor article published on November 2003.
- [37] Meléndez-Colón D. Development of novel dual-function media for treatment and separation of oils & grease from tuna wastewater. M.S. Thesis, University of Puerto Rico, Mayagüez PR, 2002.
- [38] Mendicino L., Brown P., Bergstedt M., Wismer M., Riley C. and Filson J. Copper CMP effluent treatment via ion exchange. Motorola and US Filter pp. 1-6. Austin, TX and Warrandale, PA; 1999.
- [39] Minamihaba G. and Yano H. CMP slurry and method for manufacturing a semiconductor device. US Patent 6896590, 2005.

- [40] Padilla Y. and Bogere M. Development of filtration/biotreatment scheme to recycle CMP wastewater. Paper presented at the AIChE National Meeting, San Francisco Ca., November 2006.
- [41] Peercy P. Semiconductor materials research needs for the 21st century. Publication of the National Academy of Engineering, Volume 28 (4), 1998.
- [42] Pfeffer J. Solid waste management. Prentice-Hall, New Jersey, 1992.
- [43] Pritchard P., Lin J., Mueller J. and Shields M. Bioremediation research in EPA: An overview of needs, directions, and potentials, in Biotechnology in industrial waste treatment and bioremediation. Eds. Hickey R.F. and Smith G., CRC Press, Boca Raton, FL, 3-26, 1996.
- [44] Pouet M., Persin F. and Rumeau M. Intensive treatment by electrocoagulation-flotation-tangential flow in microfiltration in areas of high seasonal population. Water Science and Technology, 25(12): 247-253, 1992.
- [45] Reker M., *et al.* Treatment and water recycling of copper CMP slurry waste streams to achieve environmental compliance for copper and suspended solids. Semiconductor Fabtech 8th ed.: 141-150.
- [46] Richardson S. Disinfection by-products and other emerging contaminants in drinking water. Trends in Analytical Chemistry, Volume 22, Issue 10: 666-684, 2003.
- [47] Rossini M., Garcia Garrido J. and Galluzzo M. Optimization of the coagulation-flocculation treatment: influence of rapid mix parameters. Water Research 33 (8), 1817-1826, 1998.
- [48] Ruiz A. and Ogden, K. Biotreatment of organic compounds and copper in waste streams from semiconductor manufacturing. NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing, 2004.

- [49] Siddiqui J., Castillo D., Kapoor R., Keefover T. and Richards R. Low defectivity product slurry for CMP and associated production method. US Patent 6979252, 2005.
- [50] Singh R., Hagerman S., Wargo C. and Roberts W. Effective dispersion of CMP slurry abrasive particles. Paper presented at VMIC Conference, California, 2006.
- [51] Stanley L. and Ogden K. Biosorption of copper (II) from chemical mechanical planarization wastewaters. *Journal of Environmental Management*, 69-3: 289-297, 2003.
- [52] Tamilmani S., Huang W., Raghavan S. and Farrell J. Electrochemical treatment of simulated copper CMP wastewater using boron doped diamond thin film electrodes – A feasibility study. *IEEE Transactions on Semiconductor Manufacturing*, 17 (3), 2004.
- [53] Tchobanoglous G., Burton F. and Stensel H. *Wastewater Engineering: Treatment and reuse*. Fourth edition, Mc Graw Hill, 2002.
- [54] Trapani T. Discussion on downflow filters. *Fluid particle separation journal*, Vol. 9, No. 1: 6-13, 1996.
- [55] US EPA. Assessment of high-rate sedimentation processes: microcarrier weighted coagulation jar tests. *Urban Watershed Management Research*. US Environmental Protection Agency, August 1999.
- [56] US EPA. Enhanced coagulation and enhanced precipitative softening guidance manual. Office of Water (4607), US Environmental Protection Agency, May 1999.
- [57] US EPA. Guide to the disposal of chemically stabilized and solidified waste. SW-872 revised. *Municipal Environmental Research Laboratory, Office of Research and Development*. US Environmental Protection Agency, Cincinnati, OH, 1982.
- [58] US EPA. Handbook for stabilization/solidification of hazardous waste, US Environmental Protection Agency, Cincinnati, OH., EPA/540/2-86/001, June 1986.

- [59] US EPA. Method 1311. Toxicity characteristic leaching procedure (TCLP), in US EPA, Test Method for evaluating solid waste, SW-846, Washington, DC Office of Solid Waste and Emergency Response, 1986, Revision July 1992.
- [60] Valenzuela F., Fonseca C., Basualto C., Correa O., Tapia C. and Sapag J. Removal of copper ions from a waste mine water by a liquid emulsion membrane method. *Minerals Engineering* 18, 33-40, 2005.
- [61] Wentz C. *Hazardous Waste Management*. McGraw-Hill, 1989.
- [62] World Health Organization (WHO), International Agency for Research on Cancer (IARC). Some metals and metallic compounds, IARC Monographs on the Evaluation of Carcinogenic Risk to Humans, Volume 23, 1998.
- [63] Yang G. and Yang T. Reclamation of high quality water from treating CMP wastewater by a novel crossflow electrofiltration/electrodialysis process. *Journal of Membrane Science*, 233(11), 151-159, 2004.
- [64] Zaidi B. and Imam S. Inoculation of microorganisms to enhance biodegradation of phenolic compounds in industrial wastewater. Isolation and identification of 3-indigenous bacterial strains. *Journal Gen. and Applied Microbiol.*, 42: 249-256, 1996.