The Environmental Impact of Copper CMP

By

Benoît MAAG

Submitted to the Department of Civil and Environmental Engineering
in Partial Fulfillment of the Requirements for the Degree of
Master of Engineering in Civil and Environmental Engineering

At the
Massachusetts Institute of Technology
June 2000

Signature of Author____________________
Department of Civil and Environmental Engineering
May 9th 2000

Certified by____________________
Duane Boning
Associate Professor of Electrical Engineering and Computer Science, Thesis Supervisor

Certified by____________________
Bettina Voelker
Assistant Professor of Civil and Environmental Engineering, Thesis Advisor

Certified by____________________
David Marks
Director, MIT Center for Environmental Initiatives, Thesis Reader

Accepted by____________________
Daniele Veneziano
Chairman, Department Committee on Graduate Studies

---

[1] The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part.

The Environmental Impact of Copper CMP

By
Benoît Maag

Submitted to the Department of Civil and Environmental Engineering on May 9th 2000 in
Partial Fulfillment of the Requirements for the Degree of
Master of Engineering in Civil and Environmental Engineering

ABSTRACT

The imminent proliferation of copper CMP, a new semiconductor manufacturing process, has prompted the need for a study of its environmental impact.

This study, focusing on the impact of copper discharged in process effluents, starts with an analysis of the manufacturing process and the modeling of plant flows and effluents. The analysis shows that copper discharged from a model facility would reach 1.25 kg per day, sludge generated would amount to 1 ton per day and effluents to 1.3 million gallons a day. Numbers may vary in plants that reuse water and at facilities that combine several manufacturing lines but copper effluent concentrations should in all cases range from 0.1 to 0.5 ppm.

A chemical model is also developed to understand copper speciation in process effluents. Tests on real samples supplied by manufacturers match relatively well the predictions from the model. A better knowledge of slurry components would be necessary to explain some discrepancies and further validate the model.

Depending on copper speciation (particulate, dissolved in weakly or strongly complexed form) in process effluents, the impact on the receiving water body in the case of direct discharge or on the operation of the receiving wastewater treatment plant (POTW) in the case of indirect discharge are evaluated.

Direct discharge should require treatment of the effluents in most cases to reach the facility's discharge limits, as specified in the NPDES (National Pollutant Discharge Elimination System) permit. Adverse effects on the environment due to copper are not expected as long as effluents are in compliance with limits specified in the NPDES permit of the facility. Sludge generated by the on-site treatment facility is not expected to produce adverse effects on the environment around the landfill where it is ultimately disposed.

Indirect discharge should not produce adverse effects on the operation of the biological stage of the receiving POTW. Nonetheless, strongly complexed copper may not be efficiently removed by the POTW and add to its effluents with a strong possibility of pushing it beyond its regulatory limits. Particulate copper may, on the other hand, end up in the POTW sludge. If that sludge is processed to make fertilizer, as is often the case at large POTWs, the increase in copper content may render the fertilizer non-compliant with land application regulations if it is already close to the limit.

It is hoped that this research will provide a helpful guide for the development of adequate CMP process effluent treatment systems or environmentally-friendly copper CMP chemicals.

Thesis Supervisors :

Duane Boning :	Associate Professor of Electrical Engineering and Computer Science
Tina Voelker :	Assistant Professor of Civil and Environmental Engineering

Acknowledgments

This project could not have been conducted without the help of many people to whom I am immensely grateful.

First and foremost, I would like to thank my advisors, Dr Duane Boning and Dr Bettina Voelker for their constant support and advice. Beyond being a renowned researcher , Dr Boning is also a very dedicated professor, always available for valuable advice. I appreciated very much that he opened his network of contacts for me. Dr Bettina Voelker is a specialist of trace metals in the environment and patiently guided the chemistry beginner that I was through the setup of the chemical work necessary for the project and the analysis of their results. Finally, I am very grateful to Dr David Marks, a strong critic who kept me on my toes from the beginning, who guided me through the definition of the project and throughout its development.

This project owes much to Professor Srini Raghavan of the University of Arizona at Tucson and his team, especially Yuxia Sun whose work was used to establish the chemical model for this project.

I am also very grateful to Walter Worth at Sematech who guided me to understand the regulatory framework around semiconductor manufacturing.

Maurice Hall at Massachusetts Water Resources Authority, Antonio Canales and Michael Nederman at Water and Wastewater Utility in Austin, Cathleen Brennan and Randal Moeller at the Sunnyvale Department of Public Works and Al Pincince at CDM taught me all I know about the issues related to the operation of wastewater treatment. Bill Bedsworth, an environmental engineering PhD student at UC Berkeley in Pr Sedlak's team was also of great help in understanding the fate of copper in the environment.

Last but not least, I also received a lot of support from semiconductor or material manufacturers, including Dr Larry Fredrickson and Wayne Bunker at Intel, Reed Content, Michael Tritapoe and Larry Duncan at AMD, Paul Lefevre at IBM/Sematech, Philippe Chelle at EKC Technologies, Daniel Urffer and Douglas Bellfy at Saint-Gobain Advanced Ceramics, Marc Tricard at Norton Abrasives, Barry Gotlinski at Pall, Josh Golden at Microbar, Doug Ward at Innovative Organics, David Volckenhauer at Degussa and Terry Francis at Applied Materials.

Finally, I would like to acknowledge the NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing which provides a very active platform for discussion and exchange between academia and industry through research projects, conferences and teleseminars.

Introduction

The demand for ever-higher integration and speed has prompted semiconductor manufacturers to shift to a new interconnect technology and replace aluminum by copper as the interconnect material for high-end logic devices. The use of the Chemical Mechanical Polishing (CMP) process that was originally developed to planarize interlayer dielectric layers (oxide CMP) was further expanded to manufacturer copper interconnects (copper CMP). This new process uses large quantities of water and generates copper, suspended solids (abrasive particles) and some organic chemicals in increased factory effluents.

The purpose of this project is to assess the environmental impact of the upcoming large-scale introduction of the CMP process.

In Chapter one, the copper interconnect technology is reviewed and the copper CMP process is presented, along with the relevant market data.

In Chapter two, a facility model is developed to represent the flows of water and process effluents in a semiconductor factory. Copper generated by the CMP process is tracked at various nodes of the facility waste collection system and the relevant regulations are explained.

In Chapter three, a chemical model is developed to understand the speciation of copper at the various nodes of the facility waste collection system and process effluents supplied by several manufacturers are tested to validate the chemical model.

In Chapter four, toxicity data on copper is briefly reviewed and the impact on the environment or on the operation of the receiving wastewater treatment plant are assessed. Copper CMP waste treatment options are presented along with the policy choices open to semiconductor manufacturers to handle this new type of waste.

Table of Contents

---

1. The Copper CMP Process

This chapter focuses on the CMP process. After a brief description of IC fabrication in Section 1.1, traditional and advanced aluminum interconnect technology as well as copper interconnect technology are presented in Section 1.2, along with the rationale for the development of copper metallization. The copper CMP process is described in Section 1.3. CMP equipment and consumables markets are presented briefly in Section 1.4.

1.1. The Manufacturing of an Integrated Circuit

The overall picture of the manufacturing of an Integrated Circuit (IC) has not changed much since its inception in the early 1970s. IC fabrication involves essentially three stages : the patterning of a network of transistors on a silicon wafer, the manufacturing of a network of connections (Interconnects) that links the various transistors together and with the 'outside world', and the packaging of the IC into a shape that can be soldered to a Printed Circuit Board (PCB) that will then be hosted into the final product (computer, automobile ignition controller, home stereo and thousands of other electronic assemblies).

The first stage of manufacturing (Front End) involves a large number of consecutive steps that are aimed at creating a pattern of doped silicon and insulator areas in the silicon that will become the network of transistors of the IC. On one single wafer, several hundred ICs are made at the same time. At this stage, a wide collection of processes are used; they are commonly referred as PEDO processes (Photolithography, Etching, Diffusion, Oxidation). The chemicals used at this stage include photosensitive resins (polymers mixed in solvents), acids (typically HF) for wet-etching and cleaning, gases (arsine, phosphine, perfluorocarbons) for doping and plasma-etching and numerous other chemicals. Considerable amounts of ultra-pure water (UPW) are also used to clean wafers thoroughly after almost each step of the process and ensure low contamination and high manufacturing yields (22 gallons per square inch of device in 1997, 4200 liters per 8-inch wafer, 1999 target 10 gallons per square inch of device) [ITRS 1998, p. 51 – Table 53].

The second stage of the process (Back End) involves the deposition and patterning of several layers of conductive metal lines (three layers for memory chips, six to seven for microprocessors in 1999) [ITRS 1998, p. 34 – Table 32]. Each layer is separated from the next by a dielectric layer (called ILD – Inter-Layer Dielectric) but connections are made between each layer and the next through holes (called via-holes or vias) filled with a conductive metal (called metal plug). The conductive metal lines are usually made of aluminum or an aluminum alloy and the metal plugs of tungsten. Nonetheless, a recent trend for high-end circuits has been to replace both with copper. A close view of an interconnect network (where the interlayer dielectric has been removed) is shown in Figure 1-1 and Figure 1-2.

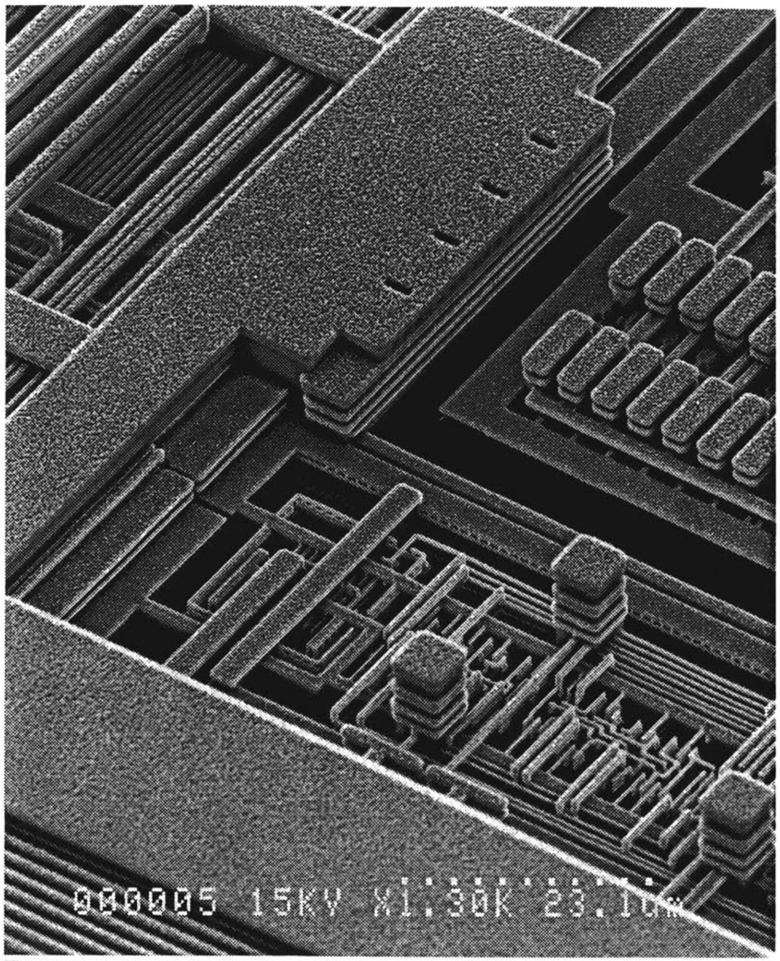


Figure 1-1 : Interconnect network [IBM WEB-1]

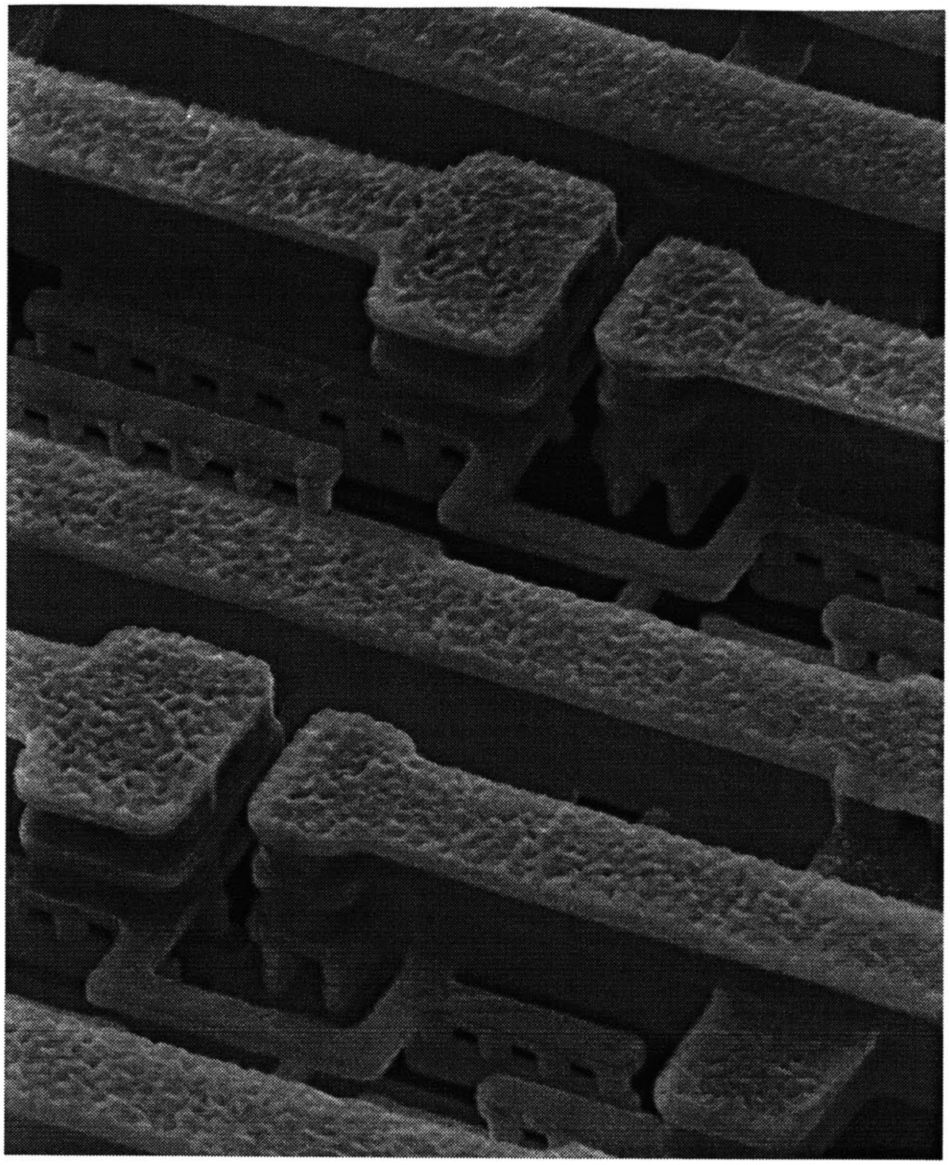


Figure 1-2 : Interconnect network [IBM WEB-1]

The last stage of the process (called packaging or sometimes also called Back-End) consists in cutting the wafer into hundreds of little squares or 'chips' that are each an IC (the dicing process), inserting them into a plastic or ceramic package, and making connections between the IC and the connection pins (Lead frame or Ball Grid Array depending on the chip packaging) to the 'outside world' that is the Printed Circuit Board.

1.2. The Manufacture of Interconnects

1.2.1. Traditional Interconnect Technology and the Development of CMP

The purpose of interconnect fabrication is to make the metal conductive lines that will link the transistors and provide connections for the input and output signals for the IC. The starting substrate is the patterned wafer. The traditional process goes as follows. First, a dielectric layer (silica or SiO_2) is deposited on the patterned wafer by spin coating of BPSG glass (first layer) or by CVD of TEOS (TetraEthylOrtho Silicate) (other layers). This layer is then patterned through a photolithography step to make via holes. A layer of tungsten is deposited by PVD (Physical Vapor Deposition); which fills the holes but also the entire surface of the wafer. Extra tungsten is removed by Reactive Ion Etching (RIE) to leave material only in the via holes. A layer of aluminum is then deposited by PVD over the entire wafer and etched so as to make the first layer of interconnects. The above process (dielectric deposition and patterning, tungsten deposition and etch-back, aluminum deposition and etch) is repeated for each layer of interconnects. In 1999, the typical number of interconnect layers is three for memory chips (Dynamic Random Access Memory or DRAMs) and six to seven for logic circuits (microprocessors) [ITRS 1998, p. 34 – Table 32]. The flow of the core process is shown in Figure 1-4and a section of an interconnect network is shown in Figure 1-3. A detailed description of the metallization process can also be found in [CHANG 1996].

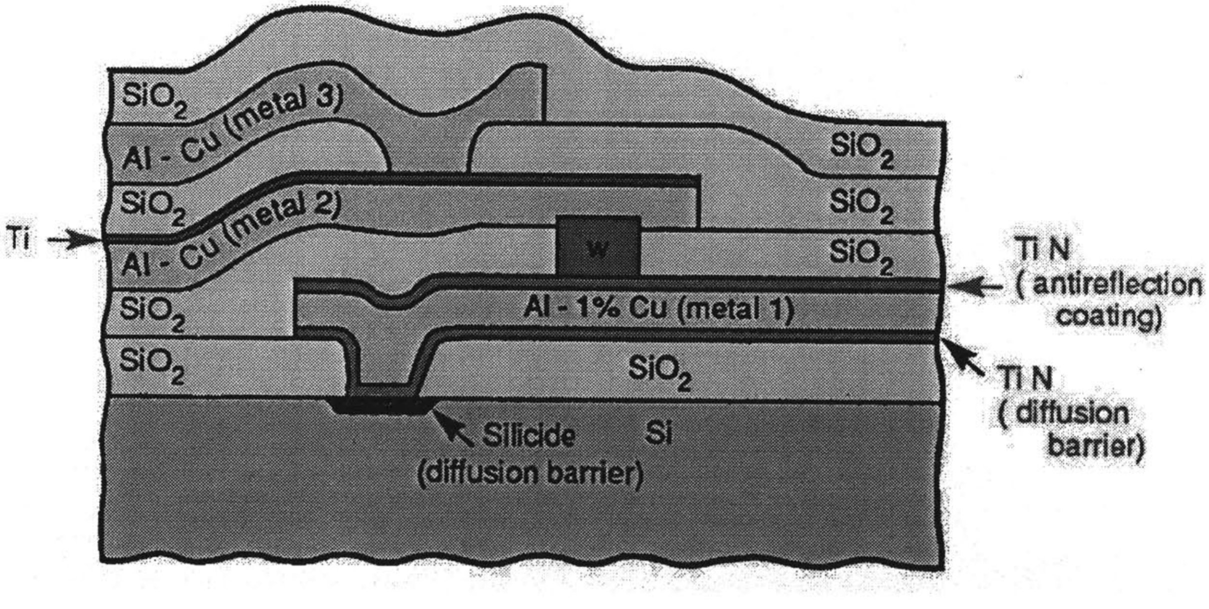


Figure 1-3 : Typical Aluminum interconnect network. Note that CMP not being used, significant topography shows in the upper levels [From THOMPSON 1993].

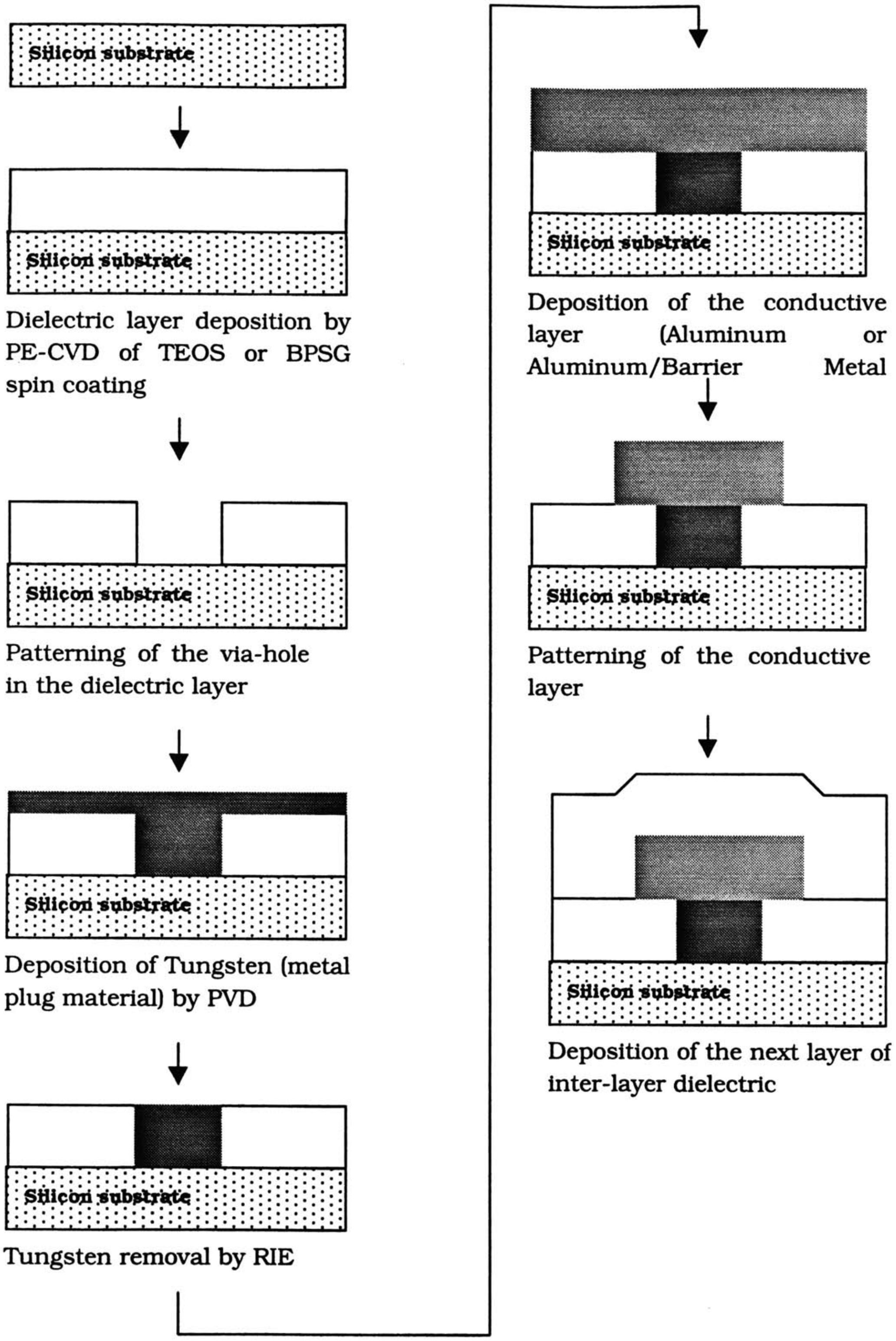


Figure 1-4 : Traditional Interconnect process flow

As can be seen on Figure 1-3, the stacking of an increasing number of interconnect layers generates hills and valleys which create design, yield and reliability problems in complex chips with small features. In order to solve these problems, IBM developed secretly in the mid-1980s a new process, Chemical Mechanical Planarization (CMP), which is a wafer-wide polishing and planarization process aimed at eliminating the hills and valleys of the dielectric (or oxide) layer. This process, made public in 1991, is called oxide CMP. A good illustration of the planarization capability of the CMP can be recognized in Figure 1-5. The advantages of this type of polishing process have since prompted the development of new applications of CMP. The RIE process for etching back the extra deposited tungsten is replaced by a CMP step (called metal CMP) and proven cost-effective and yield-enhancing [STEIGERWALD 1997, 184–187]. These developments led to the advanced aluminum technology described in Figure 1-6, where a planar surface results after each metallization layer, in contrast to the topography shown in Figure 1-3.

CMP is also used to planarize Shallow Trench Insulation (STI) structures and deep well capacitors of DRAMs. Finally, Copper CMP is an enabling technology for copper interconnect fabrication.

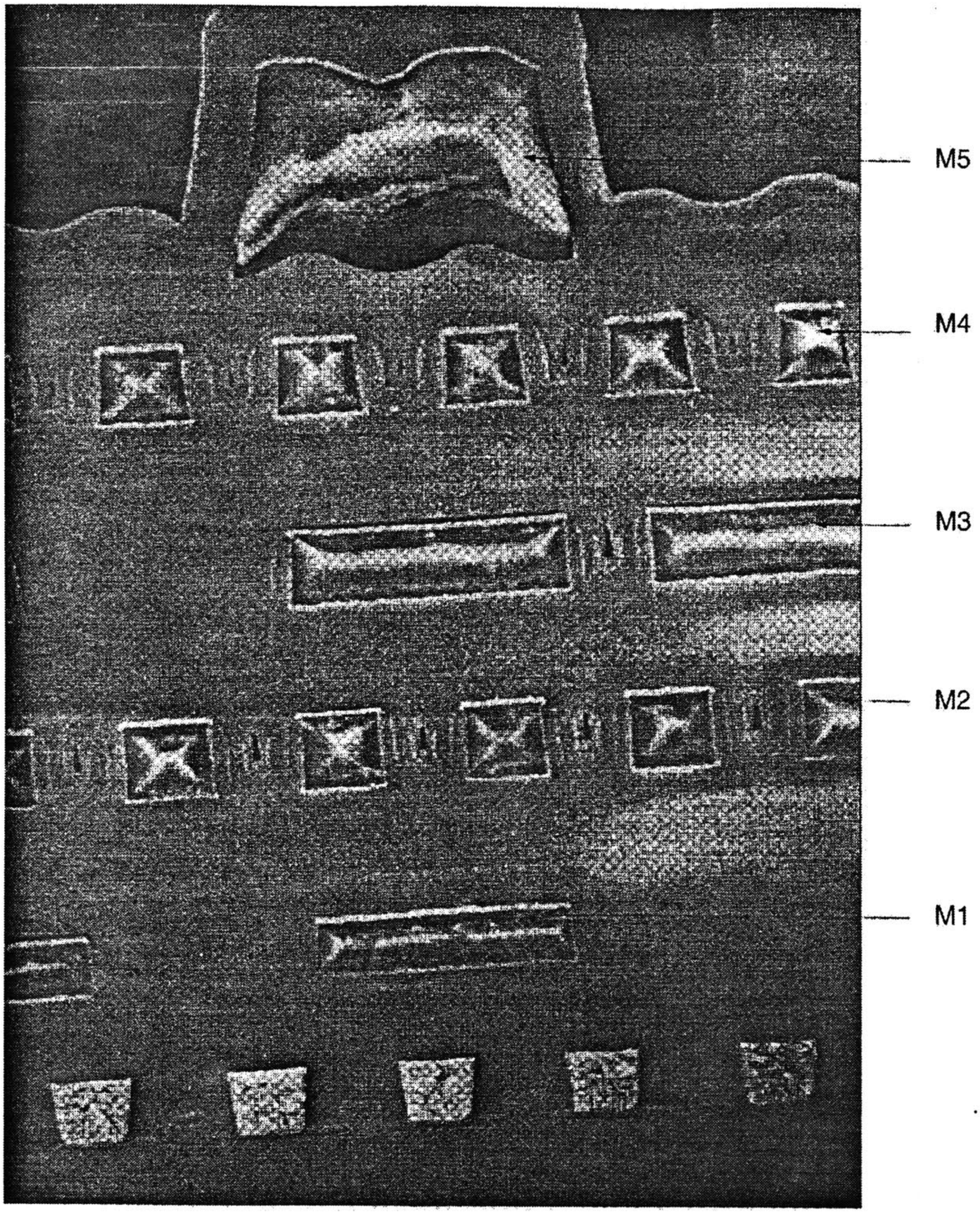
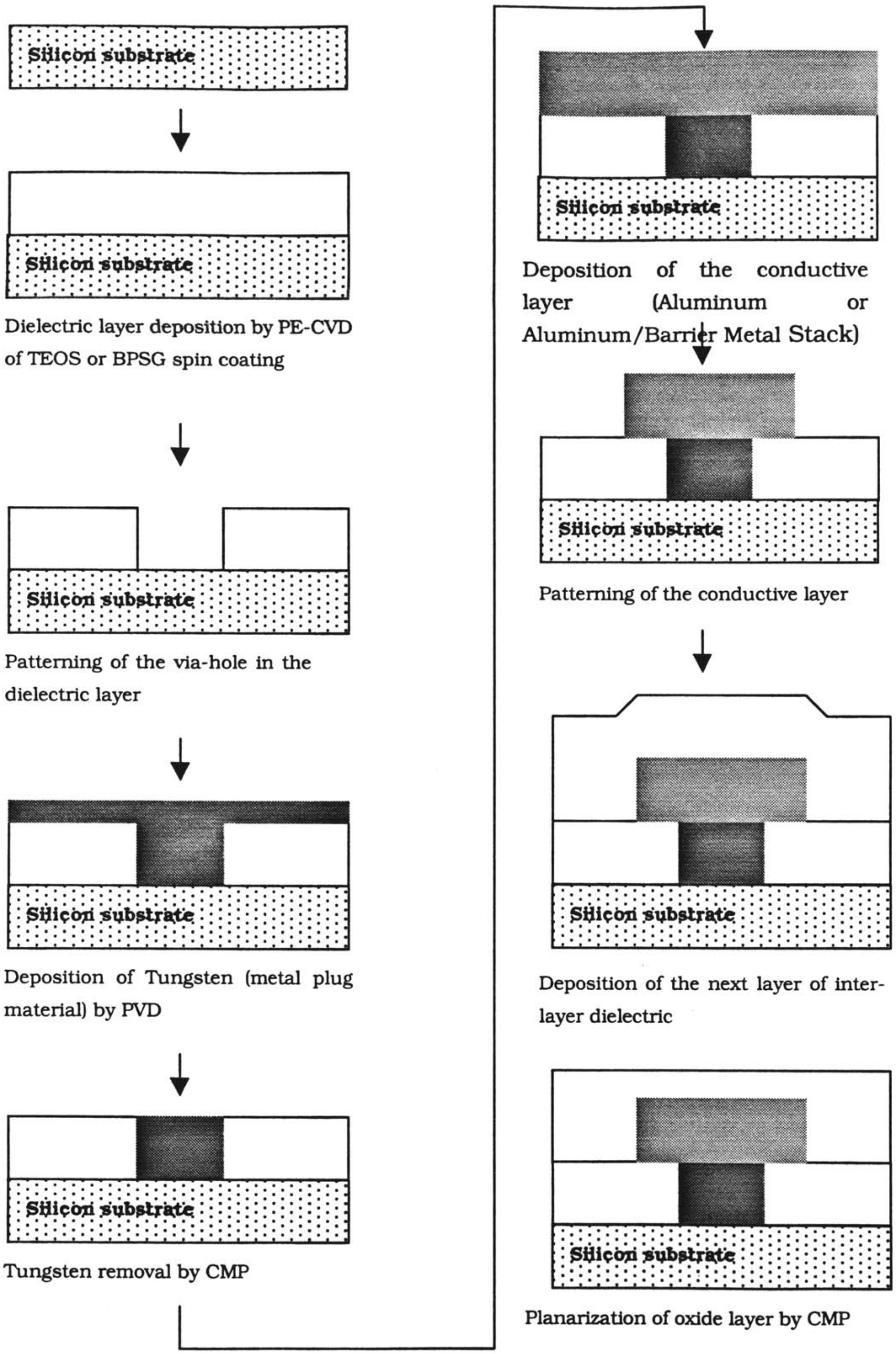


Figure 1-5 : Cross-section of an interconnect network where oxide CMP was used to planarize interconnect dielectric at all levels except that above metal layer M4.



Dielectric layer deposition by PE-CVD of TEOS or BPSG spin coating

Patterning of the via-hole in the dielectric layer

Deposition of Tungsten (metal plug material) by PVD

Tungsten removal by CMP

Deposition of the conductive layer (Aluminum or Aluminum/Barrier Metal Stack)

Patterning of the conductive layer

Deposition of the next layer of inter-layer dielectric

Planarization of oxide layer by CMP

Figure 1-6 : Advanced aluminum interconnect technology process flow

1.2.2. The Development of Copper Interconnect Technology

The original driver for the development of the copper interconnect technology was the need to increase the speed of microprocessors and other fast chips. The speed at which a chip can process information is limited by the device (transistor) delay (the time it takes for the transistor to switch to the desired state) but also by the interconnect delay (the time it takes to transfer information through the interconnect to the other relevant transistors). Though processor speed is as much a function of the hardware materials as of the design of the entire chip, a typical performance criterion is obtained by adding a typical transistor switching time with a typical interconnect delay called RC-delay. The latter is calculated by modeling an interconnect as an RC (resistor – capacitor) network. As device feature size shrinks, the cross-section of the interconnect shrinks and it becomes more resistive (increased R). Additionally, interconnects gets closer and closer to each other and they interact to form a stronger and stronger capacitor (increased C). The RC-delay, which is representative of the overall chip hardware materials performance is the product R x C. As device feature size shrinks below 1 micron, interconnect delay (the RC-delay) becomes greater than device delay and chip performance is limited by the structure of interconnects (Figure 1-7). For a detailed discussion on RC delays, see [LIN 1998].

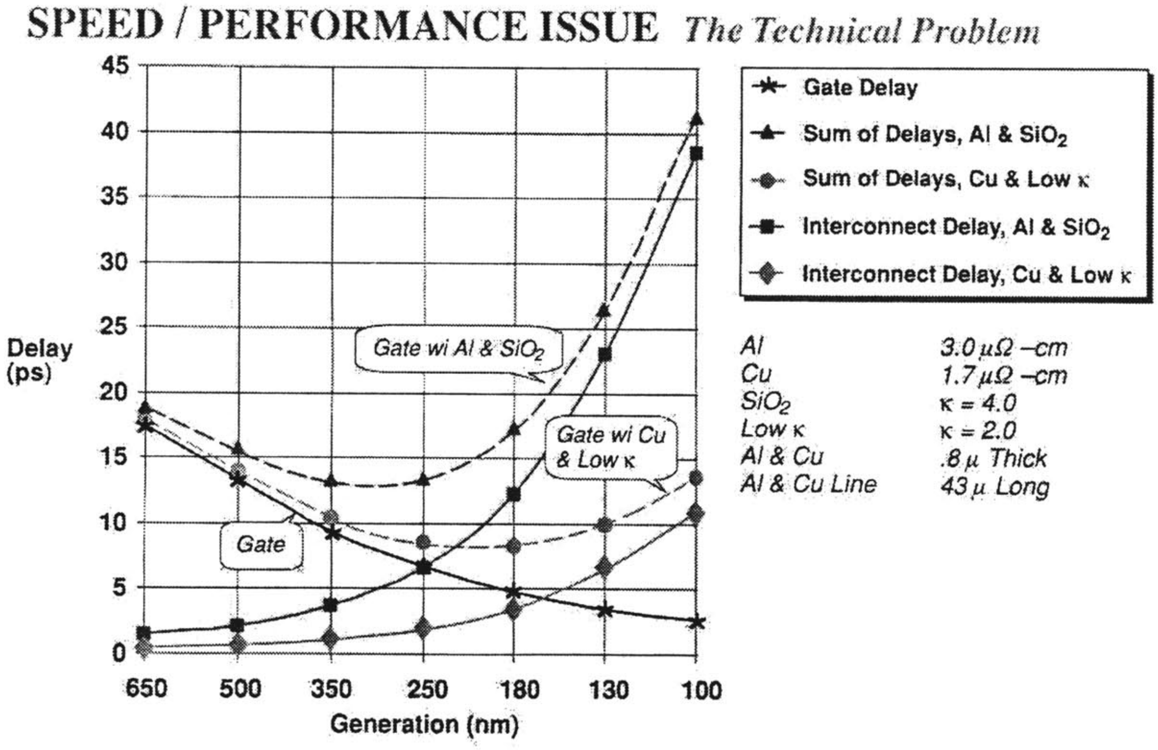


Figure 3 Calculated Gate and Interconnect Delay versus Technology Generation

Calculated gate and interconnect delay versus technology generation illustrating the dominance of interconnect delay over gate delay for aluminum metallization and silicon dioxide dielectrics as feature sizes approach 100 nm. Also shown is the decrease in interconnect delay and improved overall performance expected for copper and low κ dielectric constant insulators. [1]

Figure 1-7 : Device and interconnect delay [ITRS 1997, p. 11]

In order to make chips with ever increasing performance, using a lower resistivity metal for the interconnects as well as an interlayer dielectric material with a lower dielectric constant (called low-k dielectric) have been recognized as indispensable. Possible interconnect materials have been studied and their properties are summarized in Table 1-1. Among the possible candidates, copper was chosen because of its low resistivity and high immunity to electromigration which guarantees high interconnect reliability (electromigration is a process by which the electrons in the device, submitted to the high electric field densities, transfer momentum to the interconnect atoms and literally displace them, leading to interconnect failure – see Figure 1-8).

	Ag	**Al**	**Al Alloy**	**Au**	**Cu**	**W**
Resistivity (μΩ.cm)	1.59	2.66	~3.5	2.35	1.67	5.65
Electromigration resistance (at 0.5 μm)	Poor	Poor	Poor–Fair	Very Good	Good	Very Good
Corrosion resistance	Poor	Good	Good	Excellent	Poor	Good
Adhesion to SiO2	Poor	Good	Good	Poor	Poor	Poor
Si Deep Levels	Yes	No	No	Yes	Yes	No
CVD processing	None	?	None	None	Available	Available
RIE etch	None	Available	Available	None	?	Available

Table 1-1 : Interconnect materials properties [From STEIGERWALD 1997]

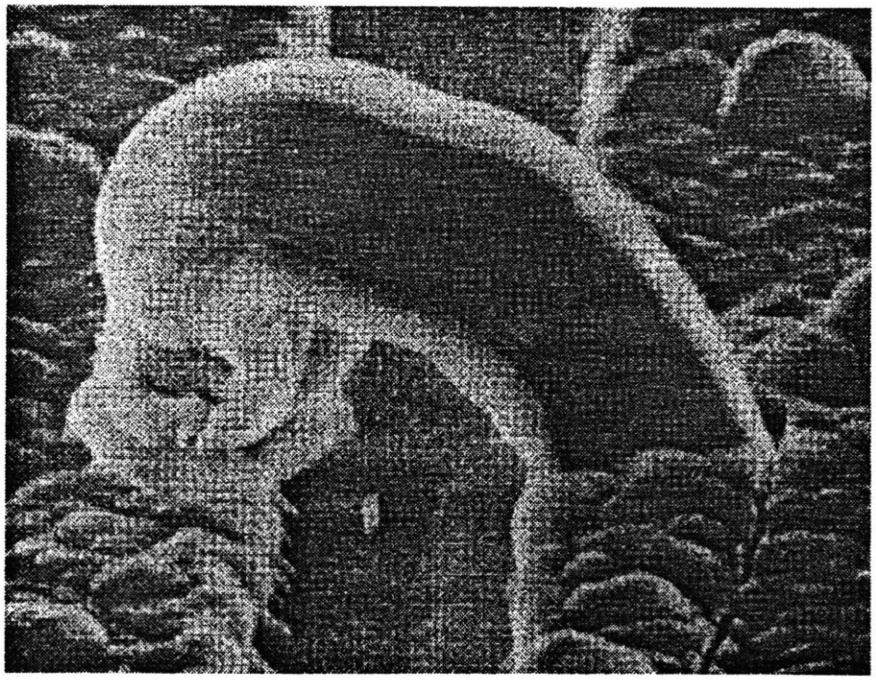


Figure 1-8 : Failure by electromigration [From DELANEY 1989]. A hillock extruded through a hole in overlying glass layer, causing a short.

Nonetheless, copper as an interconnect has two main process challenges. Firstly, copper should be perfectly isolated from the underlying silicon devices, since copper can migrate to the semiconductor and, as a deep-level impurity, adversely affect device performance. This led to the development of high-performance barrier layers to isolate copper from the silicon. Secondly, since copper is more difficult to etch than aluminum, a new way of making metals lines had to be derived. This led to the development of the damascene (now dual-damascene) process which, as a side benefit, enables the accurate patterning of very fine lines since etching can be done more precisely in silica than in metal. The manufacturing of copper interconnects is therefore significantly different from the traditional aluminum interconnect process described in Figure 1-4 or Figure 1-6, it is shown in Figure 1-9.

While developing the new copper process, manufacturers found that, aside from improving overall chip speed, this new technology had other advantages. For example, the number of process steps and related cost could be reduced, possibly by 20 – 30%, compared to advanced aluminum technology [LINEBACK 1999] [SINGER 1997] [SINGER 1998]. For example, two CMP steps (for the oxide and the tungsten via holes) could be replaced by one copper CMP step. Additionally, the lower resistivity of copper lines allows for a reduction of the size and, as a result, a tighter packing of interconnects. The number of metallization levels can therefore be reduced, bringing even more significant cost reduction [BRAUN 1999].

For a more detailed history on the development of the copper interconnect technology, the reader is referred to [STEIGERWALD 1997, Chapter two].

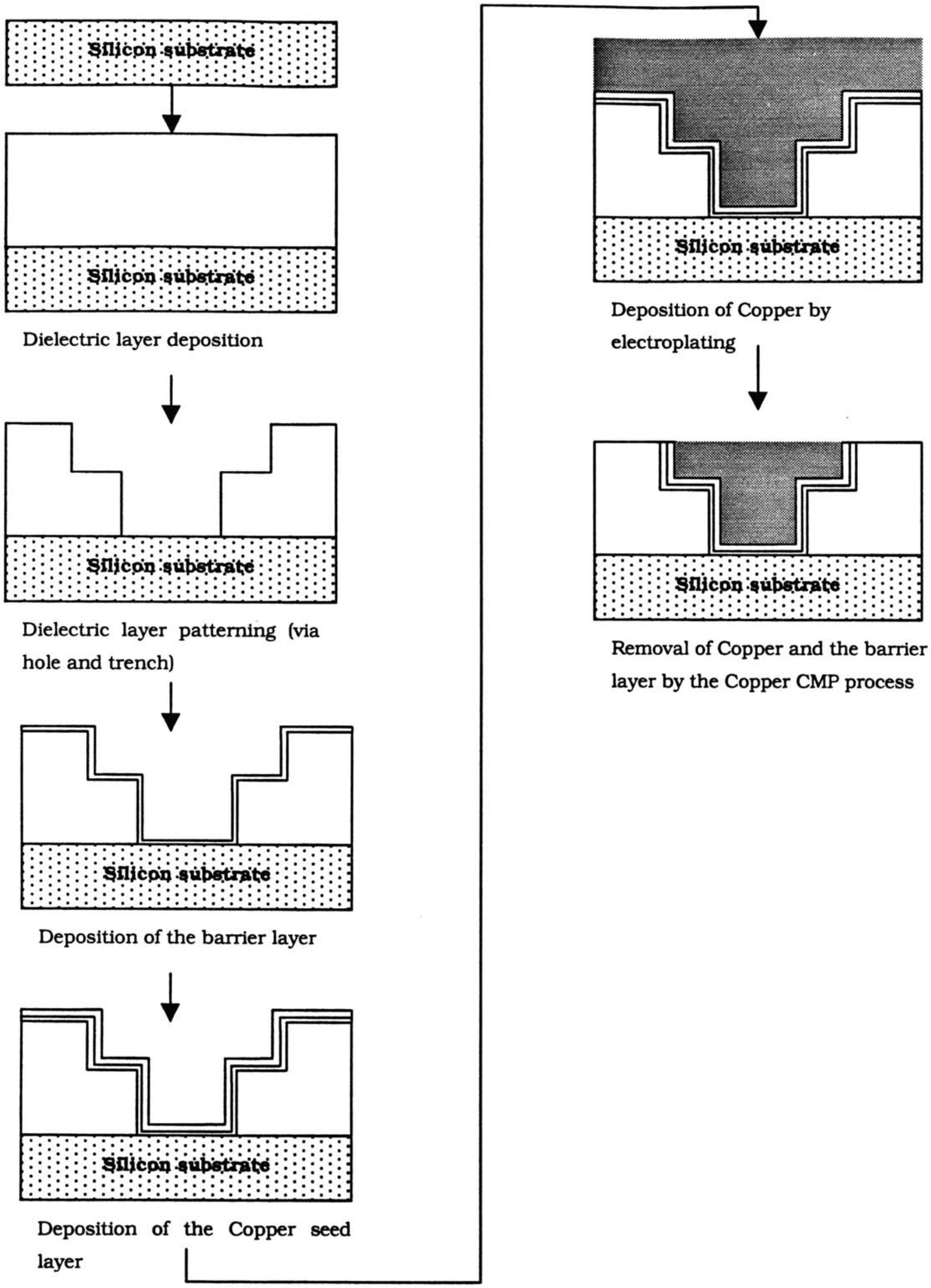


Figure 1-9: Copper interconnect technology process flow (dual damascene process)

1.2.3. The Copper Interconnect Technology

The copper interconnect technology involves the repetitive use of the dual-damascene process shown in Figure 1-9. Ultimately this process could used for all layers of metallization, though today the first layer(s) may use a combination of the traditional tungsten plug technology with a single-damascene step for the first layer of metal. This precaution is aimed at isolating the copper lines from the active semiconductor because copper, a known mid-gap impurity, may migrate to the device and contaminate it.

The first step of the dual damascene process consists in depositing and patterning a dielectric layer, typically a silicon dioxide (SiO_2) or fluorine-doped silicon dioxide (SiO_2:F). layer deposited by PECVD (Plasma-Enhanced Chemical Vapor Deposition) of TEOS (TetraEthylOrtho Silicate) precursor or by SOG (Spin On Glass). For the dual damascene process, the purpose of which is to fill via holes and interconnect lines in one step, a first layer of ILD is deposited and then covered by a thin layer (typically 300 Å) of silicon nitride which is etched so as to form the via hole layout - specifically, the nitride is removed where the via holes will be located. A second layer of ILD is deposited on top of the nitride. The subsequent process etches the interconnect trenches, stops at the underlying nitride but continues through the holes etched in the nitride layer, forming the via holes. In one etch step, the via holes and the trenches are etched through the dielectric layer.

The second step consists in depositing a barrier layer that is conductive but will prevent the copper from migrating to lower levels. This layer is usually a refractory metal or refractory metal compound : tantalum and tantalum nitride are the most common though titanium nitride or tungsten nitride have been proposed [RYU 1999]. This layer is deposited by PVD (Physical Vapor Deposition) and is typically 200 Å thick.

Above this layer, a seed layer of copper is deposited by PVD (integrated with barrier layer deposition in Applied Materials or Novellus equipment) or by CVD using a Cu(hfac)(TMVS) precusor (TriMethylVinylSilyl hexafluoroacetylacetonate Copper). The purpose of this seed is to enable the subsequent electrodeposition of copper which can proceed only if a smooth and continuous layer of copper is present.

The fourth step consists in the deposition by electroplating of the copper in the trenches and the via holes. This steps results also in an overcoat of copper on the whole wafer, the thickness of which is of the order of 0.5 – 1.0 µm.

The fifth step of the process is the CMP step, the purpose of which is to remove the excess copper and barrier layers, leaving behind the copper interconnects network.

The final step is the deposition of a silicon nitride layer that will encapsulate the copper and isolate it from the above layers.

1.3. The Copper CMP process

CMP means Chemical Mechanical Planarization, though it is also called Chemical Mechanical Polishing. It is indeed a polishing process, a 'dirty process' in an ultra-clean world, whereby a wafer is polished with an abrasive slurry. Though there are many different types of equipment used for copper CMP, we will attempt to describe a typical modern process.

A cassette of wafers (typically 25 wafers of diameter 8 inch) is loaded onto the machine. A robot picks up the first wafer and move it to the first polishing stage, where copper is removed. The wafer is stuck onto a flat plate upside down. The wafer rotates and is lowered to a rotating polishing table covered by a polishing pad. Slurry is delivered at a rate of about 200 ml per minute. Depending on process conditions, this first polishing step may last two to three minutes.

While a new wafer is picked-up from the cassette to go to the first stage of polishing, the first wafer is moved to the second stage of polishing, where the the tantalum or tantalum nitride barrier layer is removed. The process is similar to the first one but uses a different type of slurry whose chemical composition is adjusted to remove the refractory metal barrier layer.

The wafer is then moved to an optional third step while the wafers behind it follow the fabrication chain. There, dielectric buffing, i.e. surface conditioning to remove scratches, is performed.

Then, the wafer is moved to the final step. There, it is cleaned with Ultra Pure Water (UPW) and dried. This stage is very important because any particle remaining on the surface of the wafer may cause a defect and render the chip inoperable.

Finally the wafer is dried and stored onto a cassette that, when full, will be picked-up to go to the next process. A typical machine used for this process is the Applied Materials Mirra Mesa machine described in Figure 1-10.

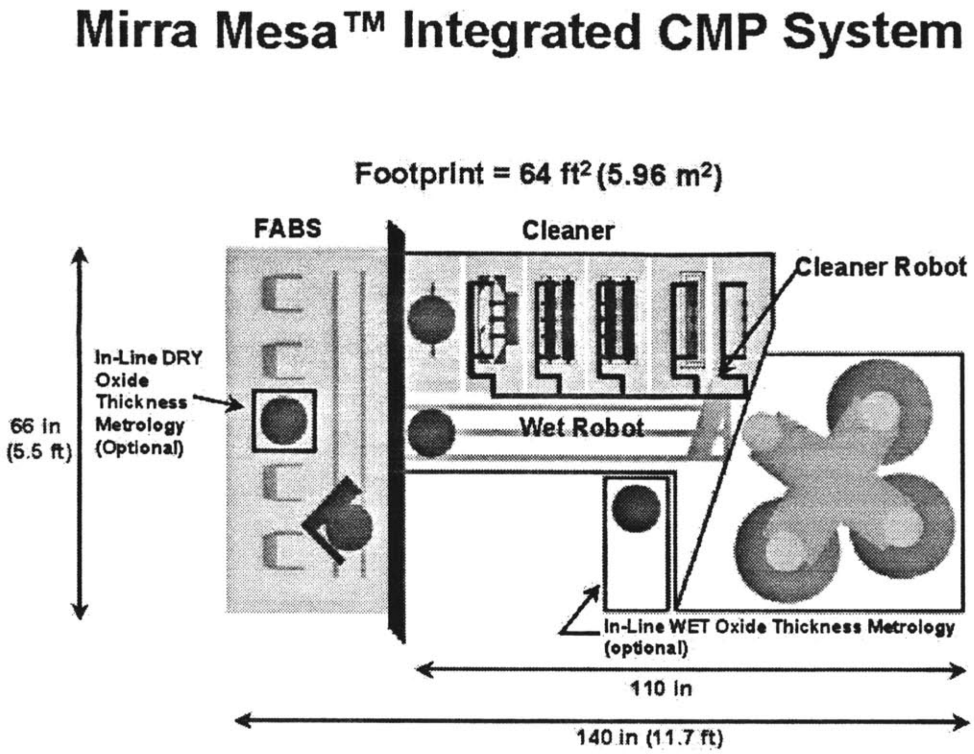


Figure 1-10 : Applied Material Mirra Mesa

1.4. The Copper CMP market

1.4.1. The Applications of Copper CMP

Since the main purpose of the development of the copper interconnect technology is to allow for an increase in chip processing speed, it is natural that the first applications of this new technology be in the microprocessor market. Indeed, IBM, Motorola and soon AMD are manufacturing their top-of-the-line microprocessors with copper interconnects. They include the PowerPC microprocessors manufactured by IBM at the Burlington, VT plant, the G3 and G4 microprocessors manufactured by Motorola in Austin TX and the new Athlon microprocessor manufactured by AMD in Dresden Germany.

Other chips that require fast processing speeds are a wide variety of ASICs (Application Specific Integrated Circuits), among which DSPs (Digital Signal Processors) are probably the most demanding in computing power. Finally, because of envisioned cost savings, it is possible that new SDRAMs (Synchronous addressing Dynamic Random Access Memories) will use copper interconnect technology, Texas Instrument being one of the pioneers.

1.4.2. The CMP Equipment Market

The market for CMP equipment is booming and Copper CMP is one of the main drivers for market growth, as seen in Table 1-2 and Figure 1-11 (for a more complete analysis, see Lehman Brothers : A brighter Polish : Trends in the Chemical Mechanical Planarization Industry, Sep. 9th 1999).

Type of CMP Application	1998	1999	2000	2001	2002	2003	2004
Oxide dielectric	360	411	455	441	392	328	267
Low-k dielectric	0	16	41	171	235	311	362
Shallow Trench Insulator	25	48	83	128	157	173	171
Passivation Layer	13	24	41	71	94	121	133
Polysilicon	6	24	52	99	110	121	152
Tungsten	215	234	258	298	282	276	248
Dual Damascene Copper	13	48	103	213	298	397	571
TOTAL	632	805	1033	1421	1568	1727	1904

Table 1-2 : CMP Equipment market trends (All numbers are in million of dollars). From [LEHMAN 1999].

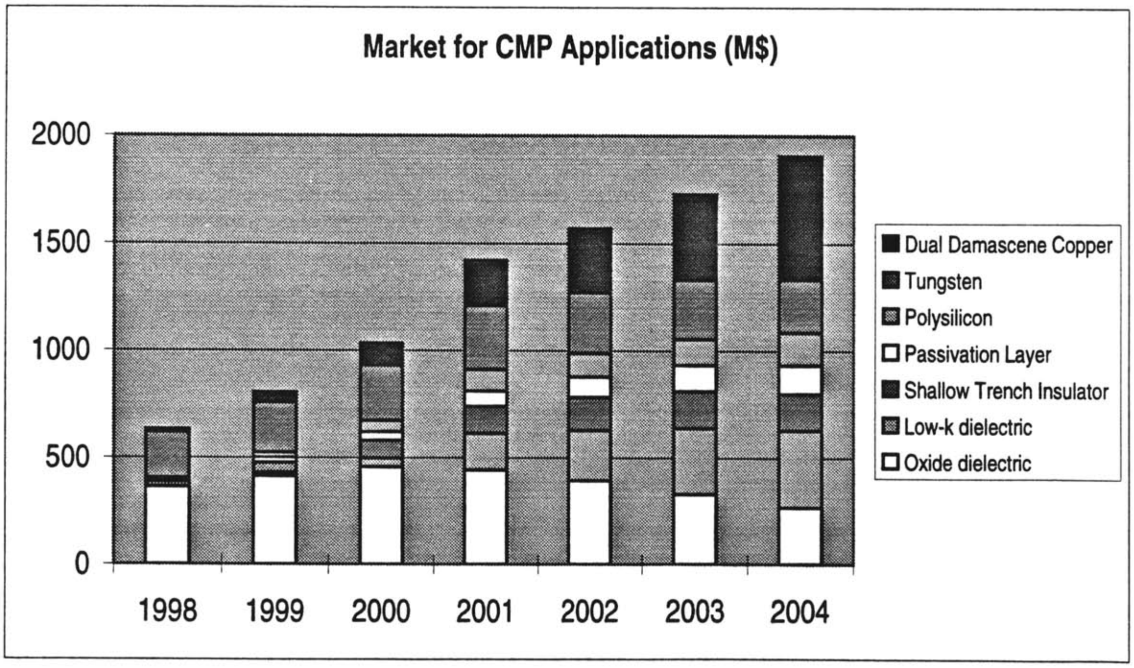


Figure 1-11 : CMP Equipment market trends. From [LEHMAN 1999].

Three companies share the major part of this $600 M+ market in 1998 : Applied Materials (37%), IPEC-Speedfam (24%) and Ebara (24%). The weight of Applied Materials has increased in 1999 to reach a 60% share. A typical high-end equipment costs $2.5 M.

1.4.3. The CMP Consumables Market

The copper CMP consumables market includes a wide range of products, ranging from hydrogen peroxide to PVA brushes. Sticking to the main, non-commodity materials used in CMP, the 1997 market was around $193 M and is expected to grow ten-fold by 2010, as shown in Table 1.3.

Material	**1997**	**1998**	**2010**
Oxide slurry	73	91	637
Metal slurry	52	61	541
Polishing pads	39	44	129
PVA brushes	12	14	65
Slurry filters	8	10	153
Other	8	10	153
TOTAL	**193**	**230**	**1677**

Table 1-3 : CMP consumables market (All numbers in millions of dollars). [From OMARA 1998].

2. Copper CMP Effluents and Their Regulatory Framework

This chapter focuses on the regulatory framework relevant to the copper CMP process.

As background information, an overview of the nature of the copper interconnect technology effluents and wastes is presented in Section 2.1.

A simple facility model, describing the overall flows and effluents of a single copper manufacturing line, is presented in Section 2.2. It will be the basis for all the further analysis developed in this study.

The US regulatory framework relevant to the effluents of the copper CMP process is described in Section 2.3. Both the cases of direct discharge (into a water body) or indirect discharge (to a wastewater treatment plant) are analysis. The regulatory framework for sludge generated from the removal of suspended abrasive particles from the effluents is also presented.

2.1. The Effluents of the Copper Interconnect Technology

The copper interconnect technology as described in the previous chapter generates a variety of effluents and wastes, solid, liquid or gaseous.

The deposition of the dielectric layer by CVD of TEOS generates effluent gases, including un-reacted TEOS [GU 1999]; additionally, the periodic cleaning of the deposition chamber is performed with a C_2F_6 plasma, a greenhouse gas that also contributes to the destruction of the ozone layer. The nitride deposition is usually a vacuum sputtering process which generates no effluents, except for those resulting in the cleaning of the nitride layer deposited on chamber parts and the sputtering targets which are usually recycled by the target manufacturer. This cleaning process is usually outsourced. Finally, the patterning of the nitride or dielectric layer is performed by a photolithography process. A thin layer of resin is spin-coated on the wafer, much of which is wasted (spun off the wafer prior to exposure) and collected for treatment outside the plant. The subsequent drying of the resin releases various solvents which are discharged into the atmosphere. Etching and stripping of the resin also generate gaseous and liquid wastes. All of these effluents and wastes are already present in the aluminum interconnect technology and will not be covered in this study.

The deposition of the barrier layer by PVD (sputtering) generates no wastes except for the waste generated by the cleaning of the chamber parts, which is outsourced, and the sputtering targets which are usually recycled by the target manufacturer.

The deposition of the copper can be done either by sputtering or by CVD of Cu(hfac)(TMVS) . Sputtering generates no wastes except for the waste generated by the cleaning of the chamber parts, which is outsourced, and the sputtering targets which are usually recycled by the target manufacturer. CVD of Cu(hfac)(TMVS) generates gaseous effluents such as un-reacted Cu(hfac)(TMVS), TMVS and $Cu(hfac)_2$ which are collected in cold traps or scrubbed. A description of the ESH (Environment Safety and Health) issues of copper deposition by CVD are presented in [ZORICH 1998].

The effluents generated by the electrodeposition of copper include the copper plating solution which is discarded after use, and plating rinse water coming from the cleaning of the wafer after the electrodeposition step. A typical deposition equipment circulates 40 gallons (150 liter) of copper plating solution (water, $CuSO_4$ and organic additives); which is discarded periodically (every week or so) and is either buried, reused or processed by electrowinning to reclaim copper. The chemistry of the plating solutions used in this process does not include Cadmium. The rinse is either directed to the plant effluent collecting tank and discharged to the POTW (Publicly Owned Treatment Works – the wastewater treatment plant) or the local stream.

The CMP process generates a complex stream of effluent, containing slurry particles and chemicals, an oxidant which is often added to the slurry at the point of use, copper oxides or chelated copper, tantalum oxide, all of it coming from the polishing and the subsequent rinses. A detailed analysis of this effluent is presented in Section 2.2.

The nitride cap layer is deposited by sputtering which generates no wastes except for the waste generated by the cleaning of the chamber parts, which is outsourced, and the sputtering targets which are usually recycled by the target manufacturer.

Finally, since many 'dummy' wafers are used for equipment tuning and even more wafers are lost due to defects, equipment malfunction, material problems and so on, a great number of wafers are reclaimed, i.e. the copper is chemically removed from the wafer with nitric acid, 'piranha' (sulfuric acid / hydrogen peroxide), ammonium persulfate / sulfuric acid or other oxidizing acid solutions. These solutions may be treated by electrowinning to remove the copper.

2.2. The Effluents of the Copper CMP Process – Manufacturing Facility Model

In order to understand the flows of copper and other chemicals in the CMP process and evaluate the regulatory or environmental issues at stake, a model is derived from data extracted from literature and obtained through discussions with semiconductor manufacturers. This model represents a single-line facility that is designed to make semiconductors with copper interconnects and includes the latest CMP technology (dry-in dry-out machines). CMP is performed in a separate area, as it is usually to prevent contamination to the front end area, and a tank collects the effluents from the complete CMP process area. Since several companies are developing systems to recycle non-process and rinse CMP water which is relatively free of suspended solids and copper [JOINER 2000], we will also consider the case where polishing effluents are segregated from post-CMP clean effluents.

The characteristics of the model facility are described below (Table 2.1).

Factory	Capacity 6300 wafer starts per week 8 inch wafers Packaging (backgrinding, dicing...) off-site
Product	Microprocessor 5 layers of copper interconnects 1st level of via hole : Tungsten plug
Polishing Processes	1 Shallow Trench Insulator (STI) 1 Pre-Metal Dielectric (PMD) 1 Tungsten 5 Copper
Equipment	20 Dry-in Dry-out CMP machines Throughput 25 wafers / hour CMP process time : 2.5 minutes for all steps Uptime 60%
CMP Processes	
STI	Silica slurry
PMD	Silica slurry
Tungsten	Silica slurry
Copper	- alumina slurry for copper removal - silica slurry for barrier layer removal - no oxide buff
Water Consumption	400 GPM of UPW for non-CMP processes 200 GPM UPW for CMP - 10 Gallons UPW / minute / CMP tool - 5 Gallons UPW / layer for polishing effluent only 300 GPM city water from TPU, scrubbers, cooling... (1) Domestic use negligible Total Consumption 900 GPM of city water (1.3 MGD) Total Consumption 29 gallons / in^2 (2) Total Effluents 900 GPM (1.3 MGD)
Slurry Consumption	200 ml / minute (total 0.5 l) for any step

Table 2-1 : Model facility parameters

(1) Collected from the reverse osmosis plant that generates UPW and has efficiency of 67%

(2) This is compatible with data from [ITRS 1998, p. 51, Table 53] that shows a water consumption of 30 gallons per in^2 in 1997. Lower numbers are shown for 1999 targets but the value of 30 gallons per in^2 is still today's actual.

We assume that 1 µm of copper is removed per polishing step. On an 8-inch wafer, that amounts to about 0.28 g of copper per copper CMP step. There are 7200 CMP steps performed per day, including 4500 copper CMP steps, generating a total of 1.3 kg of copper. From that amount and the above data, we can estimate the characteristics of the effluents at various steps of the process as follows (Table 2-2), assuming that there is no treatment of the CMP effluents.

Effluent	Copper (ppm)	Alumina (ppm)	Silica (ppm)	TSS (ppm)
Segregated Copper CMP Process Effluents	8.9	792	3958	4749
Segregated CMP Process Effluents	5.5	495	3958	4453
Copper CMP End-of-Process	1.8	158	792	950
CMP End-of-Process	1.1	99	792	891
Total Plant Effluent	0.26	23	183	206

Table 2-2 : Concentration of Copper and Suspended Solids in effluents

Then, if no treatment is performed on CMP effluents, the flows of the model facility would be as shown in
Figure 2-1. 900 GPM (Gallons Per Minute) of city water go through the UPW (Ultra-Pure Water) plant that generates water of high-purity for use in the semiconductor manufacturing processes. The yield of the UPW plant is strongly dependent on the quality of the incoming city water; a yield of 65% (a typical value for a plant in the US) was used for this study. 300 GPM of reject water from the UPW plant are supplied to non-process systems such as scrubbers or cooling towers. Among the 600 GPM generated, two thirds (400 GPM) are used by non-CMP processes and one third (200 GPM) are used by the CMP processes, 10 GPM per CMP tool. Since there are five copper CMP steps are three non-copper CMP steps in the process, five eights of the CMP flow is used by copper CMP tools (125 GPM) and the rest by other CMP tools.

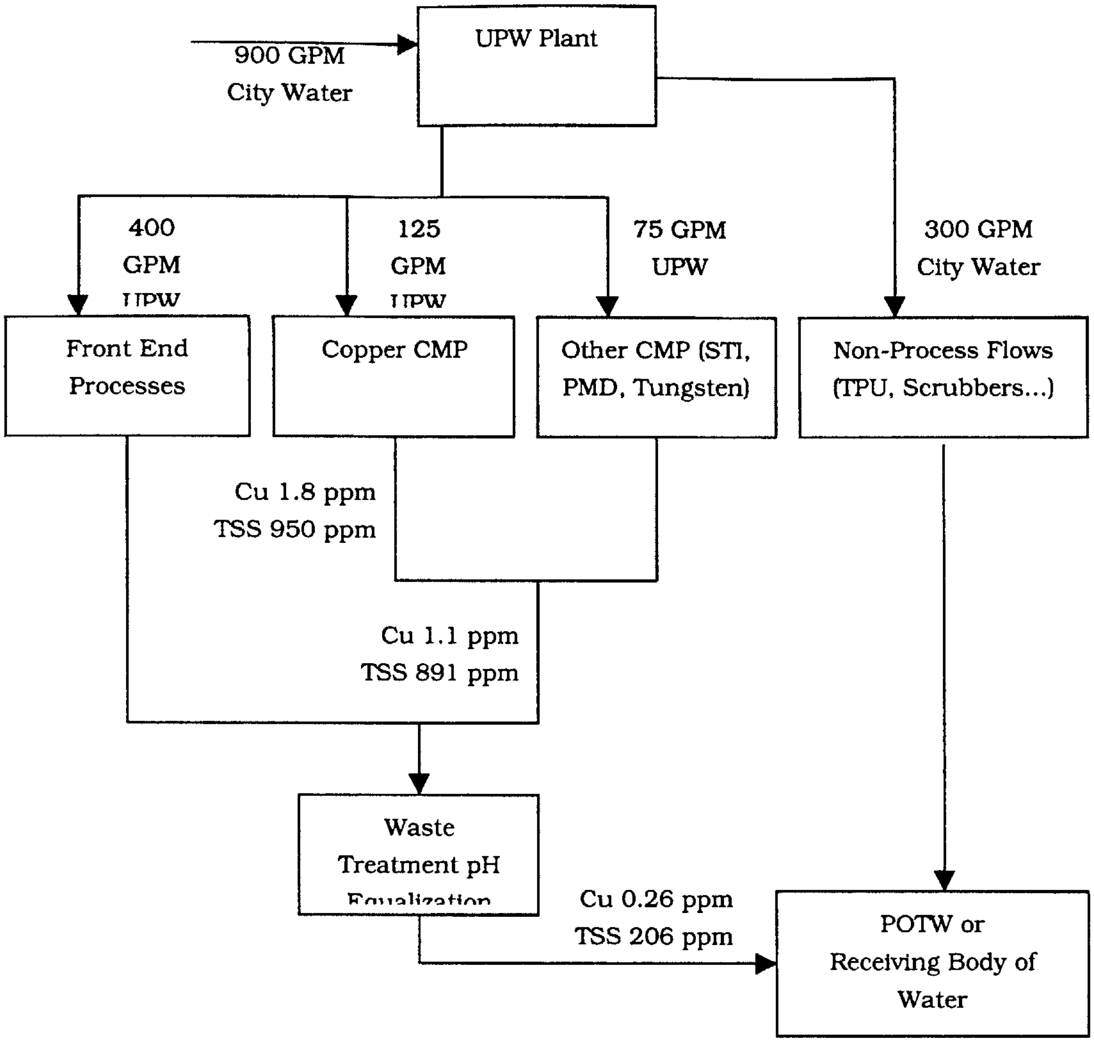


Figure 2-1 : Model facility flows (no CMP effluent treatment)

This simple model does not take into account several factors that would increase copper concentration in the final effluents, such as water re-use and recycling in the semiconductor facility or the evaporation of water in cooling towers. For example, water that is used in cooling towers evaporates so that the final quantity of effluents of the facility is somewhat smaller that the total water uptake. It is recognized that water evaporation in a semiconductor facility can range between 20% to 40% and is increased when water is re-used or recycled in the plant. This means that copper concentration in the total plant effluents could be 25% to 65% higher than the one calculated with the facility model.

Additionally, if the SIA guidelines are to be implemented [ITRS 1998, p. 51, Table 53], the water consumption per in^2 of wafer would be reduced by a factor of 3 by 2001 and by a factor of 6 by 2006. That would signify an increase of the copper concentration by a factor of 3 to 0.75 ppm and 6 to 1.5 ppm by 2001 and 2006 respectively.

2.3. The Regulatory Framework of CMP effluents

2.3.1. Background

The EPA was created in 1970 by a presidential order (under President Richard Nixon), unlike other agencies that were created by an act of Congress. EPA today has a wide range of responsibilities and powers, granted by Congress through the issuance of statutory mandates, such as the Clean Water Act (CWA) or the Toxic Substance Control Act (TSCA). Following the procedures defined in the Administrative Procedure Act (APA), EPA issues standards which apply to the whole country. Their actual implementation is either handled directly by EPA or left, partially or totally, to the States (in 1999, 44 states are mandated to handle NPDES (National Pollutant Discharge Elimination System) permits, Texas was mandated in 1999). States may also have additional State regulations regarding air or water effluents, occupational safety and health... but Federal regulation will always preempt State laws, meaning that State laws cannot be less stringent than Federal laws. All acts are listed in the Code of Federal Regulations (CFR) and the regulations regarding the Environment are listed under chapter 40 and bear a reference number in the form of 40 CFR XYZ. They can be retrieved from the National Archives and Records Administration at [NARA WEB-1].

In this analysis focusing on the environmental impact of copper CMP, occupational safety and health issues (regulated under the Occupational Safety and Health Act – OSHA) and gaseous effluents of semiconductor manufacturing that may arise from copper seed layer deposition or dielectric chamber cleaning (regulated under the Clean Air Act – CAA) will not be analyzed. Focus will be on the water effluents generated by the copper CMP process regulated under the Clean Water Act (CWA), and the disposal of sludge generated by wastewater treatment either at the semiconductor plant or at the Publicly Owned Treatment Works (POTW) regulated under the Resource Conservation and Recovery Act (RCRA). One should also note that, in case the semiconductor manufacturing effluents are discharged into a POTW, the latter is mandated to regulate what comes into its collection and treatment system and has enforcement authority.

2.3.2. The Clean Water Act (CWA or FWDCA)

The Clean Water Act has its source in the Federal Water Pollution Control Act of 1948 and the River and Harbors Act of 1899. It was amended in 1965, 1972, 1977 (which is when the act became commonly known as the Clean Water Act) and 1987. The Clean Water Act is meant to control point source discharges into navigable waters of the US (which means all water bodies and territorial seas) and basically states that any point-source discharge of pollutant is illegal unless it is done under the terms of an NPDES permit, renewed every year. This applies to all industrial facilities as well as POTWs. Pollutants are classified as conventional pollutants (see Table 2-3), toxic pollutants (see Table 2-4) and nonconventional pollutants which are neither categorized as conventional or toxic, such as ammonia, Chemical Oxygen Demand (COD) and some other organic chemicals such as pesticide residues.

Biological Oxygen Demand (BOD)	Total Suspended Solids (TSS)	PH
Fecal Coliform	Oil and Grease	

Table 2-3 : The five Conventional Pollutants (defined in 40 CFR 401.16)

1. Acenaphthene
2. Acrolein
3. Acrylonitrile
4. Aldrin/Dieldrin [1]
5. Antimony and compounds [2]
6. Arsenic and compounds
7. Asbestos
8. Benzene
9. Benzidine [1]
10. Beryllium and compounds
11. Cadmium and compounds
12. Carbon tetrachloride
13. Chlordane (technical mixture and me-tabolites)
14. Chlorinated benzenes (other than di-chlorobenzenes)
15. Chlorinated ethanes (including 1,2-di-chloroethane, 1,1,1-trichloroethane, and hexachloroethane)
16. Chloroalkyl ethers (chloroethyl and mixed ethers)
17. Chlorinated naphthalene
18. Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
19. Chloroform
20. 2-chlorophenol
21. Chromium and compounds
22. Copper and compounds
23. Cyanides
24. DDT and metabolites [1]
25. Dichlorobenzenes (1,2-, 1,3-, and 1,4-di-chlorobenzenes)
26. Dichlorobenzidine
27. Dichloroethylenes (1,1-, and 1,2-dichloroethylene)
28. 2,4-dichlorophenol
29. Dichloropropane and dichloropropene
30. 2,4-dimethylphenol
31. Dinitrotoluene
32. Diphenylhydrazine
33. Endosulfan and metabolites
36. Fluoranthene
37. Haloethers (other than those listed else-where; includes chlorophenylphenyl ethers, bromophenylphenyl ether, bis(dichloroisopropyl) ether, bis-(chloroethoxy) methane and poly-chlorinated diphenyl ethers)
38. Halomethanes (other than those listed elsewhere; includes methylene chloride, methylchloride, methylbromide, bromoform, dichlorobromomethane
39. Heptachlor and metabolites
40. Hexachlorobutadiene
41. Hexachlorocyclohexane
42. Hexachlorocyclopentadiene
43. Isophorone
44. Lead and compounds
45. Mercury and compounds
46. Naphthalene
47. Nickel and compounds
48. Nitrobenzene
49. Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
50. Nitrosamines
51. Pentachlorophenol
52. Phenol
53. Phthalate esters
54. Polychlorinated biphenyls (PCBs) [1]
55. Polynuclear aromatic hydrocarbons (in-cluding benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenz-anthracenes, and indenopyrenes)
56. Selenium and compounds
57. Silver and compounds
58. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)
59. Tetrachloroethylene
60. Thallium and compounds
61. Toluene
62. Toxaphene [1]
63. Trichloroethylene

34. Endrin and metabolites 1	64. Vinyl chloride
35. Ethylbenzene	65. Zinc and compounds

Table 2-4 : The 65 Toxic Pollutants or Classes of Pollutants (defined in 40 CFR 401.15)

A semiconductor manufacturing plant can fall into two distinct situations. Either it discharges effluents directly into a water body (for example, the IBM Burlington, Vermont plant which discharges into the Winooski river) or into a POTW (for example the Motorola Oak Hill factory in Austin Texas into the South Austin POTW).

In the first case, the semiconductor manufacturer has to obtain an NPDES permit which is issued by the State if it is mandated to do so, or by the EPA. The effluent limits are determined by an analysis of the environmental impact of the discharge. The receiving water body is surveyed by the State and the Total Maximum Daily Load (TMDL) acceptable for that water body is calculated according to 40 CFR 130. The NPDES permit limits are set so that the sum of all discharges do not exceed the TMDL and Ambient Water Quality standards are maintained. These standards are determined from toxicity studies (acute and chronic) performed on sensitive organisms in a laboratory. This analysis is conducted for the pollutants defined in Table 2.3 and 2.4 only and data is compiled by EPA in a document such as [EPA 1991-1] or [EPA 1988]. The National Recommended Water Quality Criteria for Copper are listed in Table 2-5. These criteria are merely suggestion and are not binding. States may have different critera. For example, the USGS report [USGS 1998] suggests a CCC (Criteria Continuous Concentration) of 47 ppb and a CMC (Criteria Maximum Concentration) of 59 ppb, to be compared to the suggested EPA criteria for freshwater CCC and CMC of 13 ppb and 9 ppb respectively.

	Freshwater		Saltwater	
	CMC (µg/l or ppb)	CCC (µg/l or ppb)	CMC (µg/l or ppb)	CCC (µg/l or ppb)
Copper	13	9	4.8	3.1

Table 2-5 : National Recommended Water Quality Criteria for Copper (listed in the Federal Register under 62FR42160)

Additionally, the EPA has defined categorical (industry-specific) effluent limits, such as 40 CFR 433 for metal finishing operations and 40 CFR 469 for semiconductor manufacturing operations (see Table 2-6 and Table 2-7).

Pollutant or pollutant property	Maximum for any 1 day (mg/l except for pH) (2)		Monthly average shall not exceed (mg/l except for pH) (2)	
	Metal Finishing	Semiconductor	Metal Finishing	Semiconductor
Cadmium	0.69		0.26	
Chromium	2.77		1.71	
Copper	3.38		2.07	
Lead	0.69		0.43	
Nickel	3.98		2.38	
Silver	0.43		0.24	
Zinc	2.61		1.48	
Cyanide	1.20		0.65	
Total Toxic Organics (1)	2.13	1.37	---	---
Oil and Grease	52		26	
TSS	60		31	
PH	6.0 – 9.0	6.0 – 9.0	6.0 – 9.0	6.0 – 9.0
Fluoride	---	32	---	17.4

Table 2-6 : Metal finishing and Semiconductor Industry effluent limits as defined in 40 CFR 433 and 40 CFR 469

(1) The list of TTOs is not the same for the Metal Finishing and the Semiconductor Industries

(2) Best Practical Technology (BPT), Best Achievable Technology (BAT) and Pretreatment Standards for Existing Sources (PSES) limits are the same.

Anthracene	Di-n-butylphthalate
Bis (2-ethylhexyl) phthalate	Butylbenzylphthalate
Isophorone	Carbon tetrachloride
Methylene chloride	2-Nitrophenol
4-Nitrophenol	Chloroform
2-Chlorophenol	Pentachlorophenol
1,2-Dichlorobenzene	1,3-Dichlorobenzene
Phenol	1,4-Dichlorobenzene
Dichlorobromomethane	1,1-Dichloroethane
Tetrachloroethylene	Toluene
1,1-Dichloroethene	1,2,4-Trichlorobenzene
2,4-Dichlorophenol	1,1,1-Trichloroethane
Ethylbenzene	1,1,2-Trichloroethane
Trichloroethylene	2,4,6-Trichlorophenol
Naphthalene	1,2-Diphenylhydrazine

Table 2-7 : The 30 organic chemicals regulated by the categorical standard for the semiconductor industry as Total Toxic Organics (TTO) in 40 CFR 469.12.

In the second case, the discharger must not only comply with federal and local regulations, categorical limits, sewage sludge disposal or use standards but also abide by the standards (local limits) set by the receiving POTW. The regulatory framework under which POTWs are mandated to establish and enforce local limits is called the Pretreatment Program and is discussed in Section 2.3.3.

One point also needs to be clarified. The local limits set by the POTW apply to the property-line effluent which contains mixed process effluents as well as domestic effluents (cafeteria, toilets, etc). The categorical limits apply to the end-of-process effluents. If two types of industrial processes are used on the same site, they are subject to these limits separately, i.e. they cannot be tested for pollutants after mixing (the so-called 'dilution is no solution' rule) if dilution makes a pollutant for one process non-detectable.

This was obviously an issue for semiconductor manufacturers because the electroplating and copper CMP processes were categorized as metal finishing processes (see document EPA/310-R-95-002 : Profile of the Electronics and Computer Industry, 1995, p 94). This meant that the effluents of electroplating and copper CMP should follow the metal finishing end-of-process effluent limits defined in 40 CFR 433 as 2.07 mg/l monthly average, 3.38 mg/l maximum for one day, while the semiconductor industry effluent limit for copper is not regulated under 40 CFR 469. Upon request for clarification by the semiconductor industry, the EPA issued a letter on April 21st 1998 whereby it was ruled that the electroplating and copper CMP processes would be regulated under the semiconductor industry effluent standards which set no limit on copper.

2.3.3. The National Pretreatment Program for Indirect Dischargers

The National Pretreatment Program was enacted on June 26th1978 and is found in the Code of Federal Regulations at 40 CFR 403. Its purpose is to provide the regulatory framework to ensure that non-domestic point sources do not discharge any pollutant into a POTW collection system that may (as noted in 40 CFR 403.2) interfere with the operation of the POTW (including sludge operations) or pass through the POTW, thus pushing it out of compliance of its NPDES permit and affect the ambient water quality of the receiving water body. An excellent review of the National Pretreatment Program is the EPA document [EPA 1999-2].

The Pretreatment Program controls the discharge of 126 priority pollutants (see Table 2-8), which is a sub-list of the list of the 65 Toxic Pollutants and Classes of Pollutants and can be found for example in 40 CFR 423 - Appendix A. All large POTWs (designed to treat flows of 5 MGD or more) and smaller POTWs with significant industrial discharges are required to establish a local pretreatment program. This concerned a total of 1578 POTWs as of early 1998, representing more than 80% of the national wastewater flow. The EPA has issued a number of guideline manuals that define the procedure to develop and implement local limits, such as [EPA 1983]. Essentially, the POTW will analyze its wastewater treatment pollutant removal performance data, and from it determine how much pollutant can be accepted from industrial users so as to be compliant and to avoid plant fouling. An example for allowed copper discharge is given in the Guidance Manual in section 6.1, page L-27.

001 Acenaphthene
002 Acrolein
003 Acrylonitrile
004 Benzene
005 Benzidine
006 Carbon tetrachloride (tetrachloromethane)
007 Chlorobenzene
008 1,2,4-trichlorobenzene
009 Hexachlorobenzene
010 1,2-dichloroethane
011 1,1,1-trichloreothane
012 Hexachloroethane
013 1,1-dichloroethane
014 1,1,2-trichloroethane
015 1,1,2,2-tetrachloroethane
016 Chloroethane
018 Bis(2-chloroethyl) ether
019 2-chloroethyl vinyl ether (mixed)
020 2-chloronaphthalene
044 Methylene chloride (dichloromethane)
045 Methyl chloride (dichloromethane)
046 Methyl bromide (bromomethane)
047 Bromoform (tribromomethane)
048 Dichlorobromomethane
051 Chlorodibromomethane
052 Hexachlorobutadiene
053 Hexachloromyclopentadiene
054 Isophorone
055 Naphthalene
056 Nitrobenzene
057 2-nitrophenol
058 4-nitrophenol
059 2,4-dinitrophenol
060 4,6-dinitro-o-cresol
061 N-nitrosodimethylamine
062 N-nitrosodiphenylamine
063 N-nitrosodi-n-propylamin
064 Pentachlorophenol
065 Phenol
088 Vinyl chloride (chloroethylene)
089 Aldrin
090 Dieldrin
091 Chlordane (technical mixture and metabolites)
092 4,4-DDT
093 4,4-DDE (p,p-DDX)
094 4,4-DDD (p,p-TDE)
095 Alpha-endosulfan
096 Beta-endosulfan
097 Endosulfan sulfate
098 Endrin
099 Endrin aldehyde
100 Heptachlor
101 Heptachlor epoxide (BHC-hexachlorocyclohexane)
102 Alpha-BHC
103 Beta-BHC
104 Gamma-BHC (lindane)
105 Delta-BHC (PCB-polychlorinated

021 2,4, 6-trichlorophenol
022 Parachlorometa cresol
023 Chloroform (trichloromethane)
024 2-chlorophenol
025 1,2-dichlorobenzene
026 1,3-dichlorobenzene
027 1,4-dichlorobenzene
028 3,3-dichlorobenzidine
029 1,1-dichloroethylene
030 1,2-trans-dichloroethylene
031 2,4-dichlorophenol
032 1,2-dichloropropane
033 1,2-dichloropropylene (1,3-dichloropro-pene)
034 2,4-dimethylphenol
035 2,4-dinitrotoluene
036 2,6-dinitrotoluene
037 1,2-diphenylhydrazine
038 Ethylbenzene
039 Fluoranthene
040 4-chlorophenyl phenyl ether
041 4-bromophenyl phenyl ether
042 Bis(2-chloroisopropyl) ether
043 Bis(2-chloroethoxy) methane
066 Bis(2-ethylhexyl) phthalate
067 Butyl benzyl phthalate
068 Di-N-Butyl Phthalate
069 Di-n-octyl phthalate
070 Diethyl Phthalate
071 Dimethyl phthalate
072 1,2-benzanthracene (benzo(a) anthracene
073 Benzo(a)pyrene (3,4-benzo-pyrene)
074 3,4-Benzofluoranthene (benzo(b) fluoran-thene)
075 11,12-benzofluoranthene (benzo(b) fluoranthene)
076 Chrysene
077 Acenaphthylene
078 Anthracene
079 1,12-benzoperylene (benzo(ghi) perylene)
080 Fluorene
081 Phenanthrene
082 1,2,5,6-dibenzanthracene (dibenzo(,h)anthracene)
083 Indeno (,1,2,3-cd) pyrene (2,3-o-pheynylene pyrene)
084 Pyrene
085 Tetrachloroethylene
086 Toluene
087 Trichloroethylene
biphenyls)
106 PCB-1242 (Arochlor 1242)
107 PCB-1254 (Arochlor 1254)
108 PCB-1221 (Arochlor 1221)
109 PCB-1232 (Arochlor 1232)
110 PCB-1248 (Arochlor 1248)
111 PCB-1260 (Arochlor 1260)
112 PCB-1016 (Arochlor 1016)
113 Toxaphene
114 Antimony
115 Arsenic
116 Asbestos
117 Beryllium
118 Cadmium
119 Chromium
120 Copper
121 Cyanide, Total
122 Lead
123 Mercury
124 Nickel
125 Selenium
126 Silver
127 Thallium
128 Zinc
129 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD)

Table 2-8 : Priority Pollutants (listed for example in 40 CFR 423 - Appendix A)

Logically, the local limits are unique to the POTW and are therefore dependent not only on the technology it uses or the portion of its influents that come from industry but also strongly on the receiving water body. As a result, local limits for copper can vary considerably from one location to another.

For example, the MWRA (Massachusetts Water Resources Authority) Deer Island treatment plant (Boston, MA), when it starts discharging into Massachusetts Bay, will have a dilution credit of 70:1 to meet the seawater criteria of 3.7 µg/l. By contrast, the MWRA Clinton plant (Clinton, MA) discharging into the Nashua river makes up half of the river flow and has a dilution credit of only 2:1. A more extreme case is the Sunnyvale POTW discharging into San Francisco Bay which has no dilution credit.

As a result, the local limits for wastewater set by the POTW can vary widely from one plant to another as shown in Table 2-9, ranging from 0.5 ppm to 1.9 ppm at the four POTWs considered here.

	Capacity / Average Flow MGD (1)	Water Quality Criteria for copper (µg/l or ppb)	POTW dilution credit	POTW discharge limit	POTW annual discharge limit	Industrial discharge local limit for copper
Deer Island, MA	1080 / 370	4.8 µg/l (acute) 3.1µg/l (chronic)	70:1	none	none	1.5 mg/l (2)
Clinton, MA	3 / 2.4	3.9 µg/l (acute) 2.7µg/l (chronic)	2:1	6.0µg/l (max) (3) 4.6µg/l (average) (3)	none	1.5 mg/l (4)
Austin, TX Walnut Creek	60 / 42			10 µg/l		1.9 mg/l
Sunnyvale, CA	29.5 / 15		1:1	8.6 µg/l (5)	715	0.7 mg/l (6) 0.5 mg/l (7)

Table 2-9 : Local Limits at several POTWs

(1) MGD = Million Gallons per Day
(2) Under revision, will probably be 1.0 mg/l
(3) Expected, currently under discussion
(4) Under revision, will probably be 1.0 mg/l or lower
(5) 1-Day Average
(6) Maximum Concentration, 'Grab' Sample
(7) Maximum Concentration, Composite Sample

2.3.4. Regulation on Sewage Sludge Use and Disposal

Large POTWs typically process their sludge to make fertilizer which is either sold in bulk or packaged and distributed. For example, the Massachusetts Water Resources Authority has completed a sludge-to-fertilizer plant in 1991 and is selling all its output. Such use of sewage sludge is regulated under the CWA in 40 CFR 503 that specifies some Federal limits for metal contents in 40 CFR 503.13. For example, the monthly average concentration of copper allowed under 40 CFR 503.13 is 1500 mg / kg. Additionally, States may impose stricter limits as is the case in Massachusetts where the maximum allowable monthly average concentration for copper is 1000 mg / kg.

2.3.5. The Resource Conservation and Recovery Act (RCRA)

In 1976, Congress enacted the Resource Conservation and Recovery Act (RCRA) as the primary regulatory vehicle to assure that hazardous waste is properly managed, from the point of its generation to its ultimate disposal or destruction, i.e., "from cradle to grave." RCRA establishes a very complex and comprehensive set of requirements to define the materials that are subject to hazardous waste regulation. The Act also describes the responsibilities of anyone who generates, transports, stores, treats, disposes of or otherwise manages hazardous waste. It is found in the Code of Federal Regulations under 40 CFR 240-299. An excellent orientation manual for RCRA can also be found on the EPA web site at [EPA WEB-3].

Hazardous waste identification is done according to RCRD – Subpart D (40 CFR 261.30~33) which states that a waste is hazardous if it comes from a specific process (Listed Hazardous Waste) or if it exhibits Ignitability, Corrosivity, Reactivity or Toxicity characteristics (Characteristic Hazardous Waste).

Listed Hazardous Wastes include wastes from non-specific sources, i.e. from a specific industrial operation but without specifying the technology used to perform the operation (F list defined in 40 CFR 261.31), wastes from specific sources, i.e. from a specific technology (the K-list defined in 40 CFR 261.32) and discarded commercial chemical products (the P and U list defined in 40 CFR 261.33).

Characteristic Hazardous Wastes display either Ignitability (as defined in 40 CFR 261.21), Corrosivity (40 CFR 261.22), Reactivity (40 CFR 261.23) or Toxicity (40 CFR 261.24). In order to determine whether a waste is a characteristic hazardous waste for Toxicity, a standard test called the TCLP (Toxicity Characteristic Leaching Procedure) has to be performed on a representative sample of the waste. If at least one of the 40 chemicals listed (D-list in 40 CFR 261.24) is present in excess of the regulatory level, the waste is considered a Characteristic Hazardous Waste. The D-list contains several metals (Arsenic, Chromium, Lead, Mercury, Selenium, Silver) but not Copper.

In addition, the 'mixing rule' states that any Listed Hazardous Waste mixed with a non-hazardous waste becomes a Listed Hazardous Waste and that a Characteristic Hazardous Waste mixed with a non hazardous waste remains hazardous if it exhibits any of the Ignitability, Corrosivity, Reactivity or Toxicity characteristics.

Among the Listed Hazardous Wastes, F-006 contains 'Wastewater treatment sludges from electroplating operations except from the following processes: (1) Sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc-aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum'.

The implication for waste generated by the copper interconnect process is that if rinse water from the copper electroplating process finds its way to the semiconductor factory waste treatment facility, the sludge generated becomes a Listed Hazardous Waste under F-006, no matter how little copper the sludge contains.

2.3.6. The Project XL program

Launched in 1995 by President Clinton, the Project XL scheme is aimed at introducing regulatory flexibility. As defined by EPA, Project XL, which stands for "eXcellence and Leadership," is a national pilot program that allows state and local governments, businesses and federal facilities to develop with EPA innovative strategies to test better or more cost-effective ways of achieving environmental and public health protection. In exchange, EPA will issue regulatory, program, policy, or procedural flexibilities to conduct the experiment. More information about the project XL guidelines and about specific projects can be found on the EPA web site at [EPA WEB-5].

Essentially, the idea for Project XL is that, since 'in many cases companies know their business a whole lot better than the Government does' (President Clinton, 1995), companies should be allowed regulatory flexibility provided that the outcome of the project is recognized as beneficial by the EPA. In concrete terms, a project is a trade at a specific manufacturing site of a regulatory exemption against a sometimes mixed-batch effort to reduce environmental impact of the site. Strongly criticized under the motto 'if it isn't illegal, it isn't XL' [MAZUREK 1999], it is argued that for a fast-moving industry such as semiconductor manufacturing, facing worldwide competition and introducing 100 new chemistries in manufacturing per year, regulatory flexibility is necessary to keep an edge over competition from other countries.

Several semiconductor manufacturers have applied for a project XL, including Intel for its Chandler, AZ factory and IBM for its Burlington, VT factory. The interesting point is that the latter project calls for an exemption from the F-006 regulation for the factory sludge against a reduction in greenhouse gases emissions during the dielectric chamber deposition cleaning process. It is argued that F-006, written with large-scale electroplating operations in mind should not apply to sludges where minute quantities of copper have been introduced through the mixing with plating rinse waters. Information on this project can be found on the EPA web site at [EPA-WEB 5].

2.3.7. The Superfund Act (CERCLA)

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), known as the Superfund Act, was enacted on December 11th 1980. It established a $1.6 billion dollar federal fund to pay for the clean-up of hazardous waste sites. In order to be eligible for clean-up, a site has to be identified, evaluated through the Hazardous Ranking System with a score of 28.5. Then it is listed in the National Priority List (NPL) and action for remediation is taken. At that stage, the EPA can sue the PRP (Potentially Responsible Party) to collect money for the clean-up. Among the PRPs are the generators of the substances that have polluted the site.

Sludge generated from a semiconductor facility is converted to solid waste before it can be disposed of in a landfill. Provided it has not been in contact with electroplating rinse effluents and that it does not exhibit any hazardous characteristic (Ignitability, Corrosivity, Reactivity and Toxicity), such solid waste can be disposed of in a non-hazardous landfill. Nonetheless, the semiconductor manufacturer remains liable for damages due to the waste under RCRA's principle of 'liability from cradle to grave'. Thus, there remains a possibility that, in a distant future, the receiving landfill may leach copper and be listed as a superfund site requiring clean-up. This was for example the case of several landfill sites where copper contamination has been found. They include, for example, the Sanitary Landfill Co. site in Dayton, Ohio [EPA WEB-1] or the Spickler landfill in Spencer, Wisconsin [EPA WEB-2]. Both sites were operated as municipal and industrial landfills. Even though, as was the case for the above cited superfund sites, the NPL listing may be justified by contamination by chemicals other than copper (cadmium, lead), the EPA may decide to sue the semiconductor manufacturer for clean-up costs that generally amount to millions of dollars.

2.3.8. Trends in Regulation

Several factors influence the evolution of environmental regulations. As more scientific evidence is gathered, a certain chemical may be recognized as toxic and new laws may limit its use or disposal. Additionally, as waste treatment technology improves, the EPA may require more stringent discharge limits. The public opinion and national or international political pressure may ask for a reduction of certain categories of waste. Locally, new environmental conditions (such as population growth) or the increase of certain categories of pollutants in industrial or domestic waste streams may force POTWs to revise their local limits so as to remain in compliance with the specifications of their NPDES permit and maintain ambient water quality. Currently, several new regulations relevant to copper discharge are under discussion.

The first item is the discussion currently under way between the semiconductor industry and the EPA for the declassification of sludge that has been exposed to electroplating rinse water from the F-006 listing. This would incur significant savings for the semiconductor manufacturers since disposing of hazardous waste costs typically $500 per ton whereas disposing of non-hazardous sludge costs $50 per ton. On the other hand, there is currently a debate as to whether the copper CMP sludge, seen as a follow-up of the electroplating process, should justify an F-006 rating. Semiconductor manufacturers, most notably IBM Burlington plant, VT, argue that it should not be regulated as such. EPA Region 1 (covering Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont) agrees with this view but the semiconductor industry is currently seeking guidance from the EPA on this point.

The second item concerns possible new categorical limits for the Metal Plating and Machining industry (called new MP&M). After surveying 2000 metal plating and machining sites, EPA has determined that the Best Achievable Technology economically feasible (BAT) is capable of reaching an effluent level for copper of 0.6 mg/l and for Total Suspended Solids (TSS) of 38 ppm. That limit, much stricter than any previous limit, could be applied to new and existing sources. It remains to be clarified whether it would apply to the CMP effluent process since it has been established by EPA that copper CMP is to be regulated under the semiconductor categorical standard. If new BAT limits were to be imposed on CMP effluents, efficient copper abatement technologies would have to be considered.

The last item is the EPA's approval of toxicity tests on site water rather than on laboratory water. The point is that site water contains more organic matter than laboratory water and complexes copper ions, making them less toxic to wildlife. Indeed, labile copper forms (free cupric ion and inorganically complexed copper) are toxic at low (nanomolar) concentration while copper complexed with organic matter is not. For example, MWRA tests have shown that copper was less toxic before than after the Clinton wastewater treatment plant [HALL 2000]. This result is explained by the fact that the Clinton plant releases organic carbon that binds to copper and makes it less toxic. Such tests may help raise Ambient Water Quality Standards for copper in the future, especially for POTWs that may in turn loosen their local standards for industrial dischargers. Nonetheless, one might consider that a drop in pH further downstream (due for example to the influx of a mining industry effluent) may extract copper from complexing agents and render it more toxic.

Finally, one must consider that, as Copper CMP becomes a mainstream technology, the increased load of copper and TSS into effluents may require the receiving POTW to decrease the local limits for copper. As an example, the Sunnyvale POTW has an annual discharge limit for copper of 715 pounds, or 324 kg. A facility such as the model facility described above (without CMP effluent treatment) would release 0.26 ppm of copper, which is below the current local limit of 0.5 ppm, but the total mass of copper would amount to 460 kg per year. Even with a removal performance of 85 % (a typical number, which is nonetheless dependent on copper speciation in the influent – see Section 4.4), the POTW would increase its annual discharge by about 70 kg and be driven above its limit, thus prompting a decrease in industrial discharge local limits for its customers.

2.3.9. Summary of Regulations

Figure 2-2 summarizes the regulatory requirements for the model facility described above. It is assumed that a CMP effluent system is installed and that it generates a sludge.

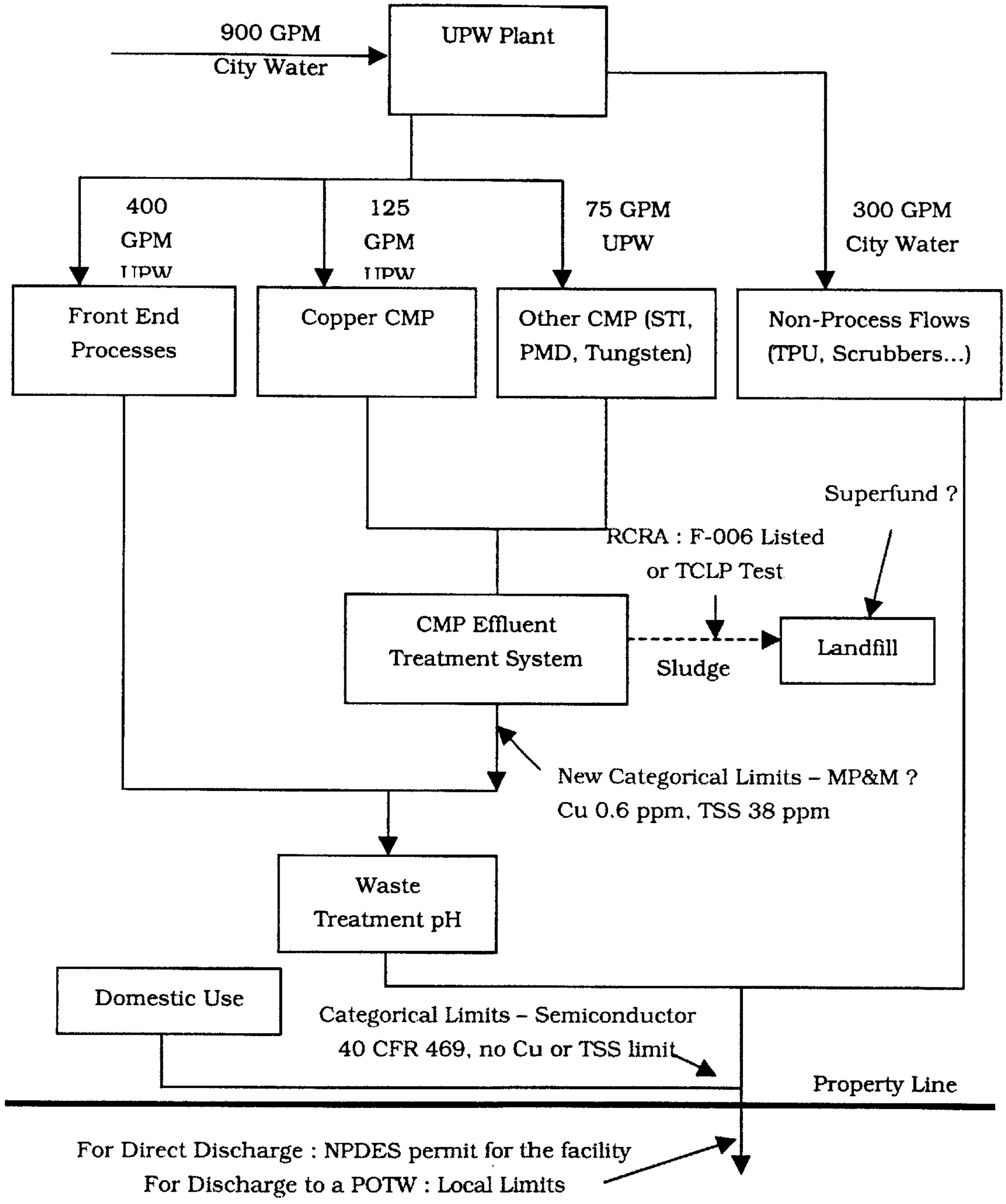


Figure 2-2 : Summary of Regulations for the model facility with CMP effluent treatment

3. The Characterization of Copper CMP Effluents

This chapter focuses on the speciation of copper at various nodes of the semiconductor facility effluent collection system, at the discharge point and in the wastewater collection system. The rationale for this analysis stems from the need to understand copper speciation in order to install an adequate waste treatment system or to assess the impact of effluents on the receiving water body or wastewater treatment plant.

A chemical model of copper speciation is described in Section 3.1. Complexation, adsorption on slurry particles and precipitation of non-soluble copper species are considered.

In Section 3.2, the chemical model is coupled with the facility model developed in Section 2.2.1 to predict the speciation of copper at various nodes of the factory waste collection system.

Experimental work performed on spent slurry samples is described in Section 3.3. Results and discussion are presented in Sections 3.4 and 3.5 respectively.

3.1. Chemical Model

The chemical model described below is based on the work of Pr Srini Raghavan at the University of Arizona at Tucson. Its purpose is to understand how the different components of the copper CMP slurry and of the different slurries that will eventually be mixed with copper CMP effluents determine copper speciation.

3.1.1. Model Slurries

Slurry components are a trade secret and are not generally known. However, the analysis of the slurry's function and related knowledge from other industry sectors where metal finishing or polishing is applied can help define the chemical boundaries of a slurry system (see Table 3-1).

Chemical	Dosage	Function
PH stabilizing acid Citric acid	pH around 3.5	Keep pH at the desired level throughout the CMP operation
Oxidant Hydrogen peroxide Iodate Hydroxylamine	An optimal value exists. Several % is a typical value	Oxidize copper since copper oxide (Cu^{II}) is more readily polished away by the abrasive particles than metallic copper (Cu^{0})
Abrasive particles Alumina, 200 nm	3 – 7 % wt at point of use	Abrasion of the copper oxide layer
Surfactants	Depending on micelle size, 300 – 1000 ppm	To keep the abrasive particles suspended
Complexing agent EDTA, EDA, Citrate	Appropriate amount to complex copper at removal location	To allow for larger quantities of dissolved copper to be carried away by the spent slurry flow
Corrosion inhibitor Benzotriazole (BTA)	75 ppm is a typical value	To avoid unwanted corrosion of copper

Table 3-1 : Typical components of a copper CMP slurry (for the copper removal step as described in Section 1.3)

For the sake of simplicity, the copper CMP model slurry that will be used for calculations will not contain any corrosion inhibitor or surfactants. It will be made as follows (Table 3-2) :

Chemical	Dosage
Alumina abrasive particles, 200 nm	5 % wt
Oxidant : Hydrogen peroxide	5 % volume
Complexing agent (optional) : EDTA or citrate	1:1 molar balance with copper removed at tool level (9.10^{-3} M)

Table 3-2 : Model copper CMP slurry (for the copper removal step as described in Section 1.3)

At tool level, concentrated slurry polishes copper at an estimated rate of 0.28 g of copper for 0.5 liter of slurry. At this stage, the maximum copper concentration is then about 560 ppm, or 9.10^{-3} M. Three types of slurries will be modeled. The first one (labeled Type A) contains no complexing agent and the pH stabilizing acid will be assumed not to bind with copper. The second one (labeled Type B) contains 9.10^{-3} M of Citrate as a complexing agent. The third one (labeled Type C) contains 9.10^{-3} M of EDTA.

The model slurry for barrier layer (Ta or TaN) removal (see Section 1.3) is silica-based (50 nm colloidal silica) with 25% wt silica content at point of use. It also contains an oxidant and is often highly acidic. It will be assumed that it has the same oxidant and pH as the copper polishing slurry.

Other slurries are modeled as colloidal silica slurries (50 nm particles) with 25% wt silica content at point of use, though fumed silica with particles shaped as strings of pearls (diameter 50 nm and length 200 nm) are often used for oxide CMP with a point-of-use concentration of 8-15% wt. The pH of oxide or STI slurries is high (around 11.5) and that of Tungsten slurries is usually low.

3.1.2. Copper Speciation

The first step in this analysis is the determination of the copper oxidation state in the effluents. This can be done with so-called Pourbaix diagrams such as the one for the copper - water solution shown in Figure 3-1. More complex diagrams including other components have been studied by Pr Srini Raghavan at the University of Arizona at Tucson and can be found in [RAGHAVAN 1999].

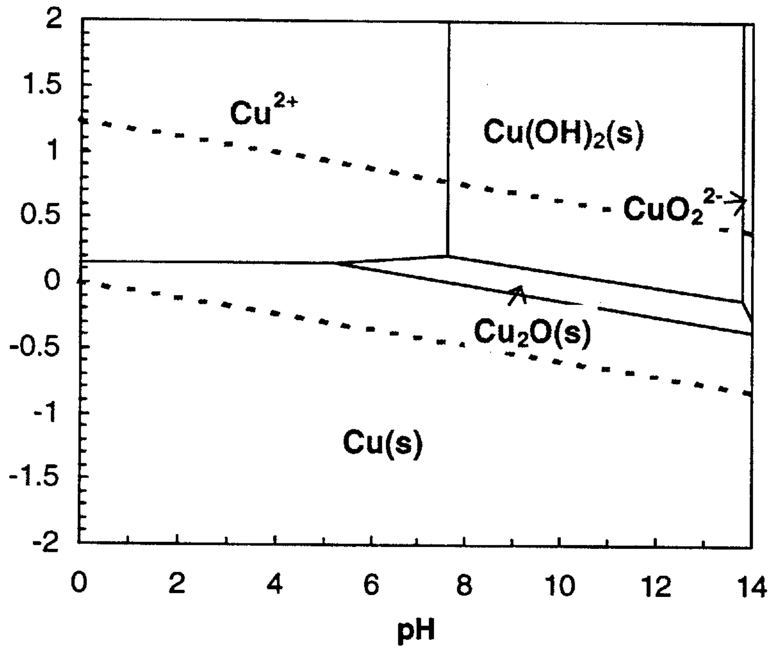


Figure 3-1 : Pourbaix diagram for copper – water system [SUN 2000]

Nonetheless, one should realize that reduction-oxidation reactions can be slow and that the redox potential of a chemical solution is defined only for equilibrium conditions. The redox potential can therefore be precisely defined and measured in systems which have been stable for a long time but it may not be the case for process effluents which are mixed and modified over a short time scale. In this analysis, the simplifying assumption that copper is in the +II oxidation state will be made in view of the fact that copper rapidly oxidizes to that level in most aerated aqueous systems and in the environment. Indeed, copper at the +I oxidation state is rather unstable in the environment and can be stabilized only under certain conditions, for example by the formation of Cu_2O or CuCl precipitates. In this analysis, it will be assumed that copper is oxidized to the +II oxidation state by the oxidant (hydrogen peroxide, iodate or hydroxylamine) and remains so. One comment should be made on the use of hydroxylamine. Though an oxidant for copper at low pH, hydroxylamine becomes a reductant for copper at higher pH, so that copper may return to the Cu^0 oxidation state as process effluents become diluted and pH is neutralized. The study of Pr Raghavan in [RAGHAVAN 1999] shows a redox potential for a hydroxylamine slurry that varies from 0.291 V at pH = 3.8 to 0.065 V at pH = 6.4. For reference, the redox potential of the Cu^{2+}/Cu couple is 0.2239 V and is independent of pH.

This analysis will therefore be limited to Cu^{II} species, namely Cu^{2+} free cupric ion, Cu^{II} complexes, precipitates and adsorbed species. The complexes and precipitates taken into account in this study are listed in Table 3-3 with their relevant chemical constants taken from [MOREL 1993, pp. 332-342]. Optional EDTA or citrate complexing agents are also listed and their effect will be taken into account in copper speciation if they are present. Precipitates are listed with a '.s' subscript.

Complexes	**Stability constant (log β)**	**Complexes**	**Stability constant (log β)**
With OH^-		**With EDTA**	
$Cu(OH)^+$	6.3	Cu:EDTA	20.5
$Cu(OH)_2$	11.8 / 14.3 (1)	CuH:EDTA	23.9
$Cu(OH)_4^{2-}$	16.4	CuOH:EDTA	22.6
$Cu_2(OH)_2^{2+}$	17.7	**With Citrate**	
$Cu(OH)_2$.s	19.3	Cu:Cit	7.2
$Cu(OH)_2$.s	20.4	CuH:Cit	10.7
With CO_3^{2-} (2)		CuH_2:Cit	13.8
$CuCO_3$	6.7	CuOH:Cit	16.4
$Cu(CO_3)_2^{2-}$	10.2	Cu_2:Cit_2	16.3
$CuCO_3$.s	9.6	**With Ammonia**	
$Cu_2(OH)_2CO_3$.s	33.8	$Cu(NH_3)^{2+}$	4.0
$Cu_3(OH)_2(CO_3)_2$.s	46	$Cu(NH_3)_2^{2+}$	7.5
		$Cu(NH_3)_3^{2+}$	10.3
		$Cu(NH_3)_4^{2+}$	11.8

Table 3-3 : Copper species and their chemical constants

(1) There are two values available in the literature for the formation constant of the $Cu(OH)_2$ complex. 14.3 is found in [NRIAGU 1979, p. 92] and 11.8 in [STUMM 1996, p. 327]. The reason for this discrepancy is probably related to the definition (or existence) of colloidal particles of $Cu(OH)_2$. Earlier data would reflect a larger amount of $Cu(OH)_2$ measured as dissolved while newer data assumes that a lot of what was formely called 'dissolved' was actually colloidal, i.e. solid $Cu(OH)_2$.s, particles. For the simulations conducted in this

study, we used the newer value 11.8. This choice is debatable since small colloidal particles may often behave as dissolved species.

(2) The formation of carbonate species due to the dissolved CO_2 from the atmosphere (dissolved or precipitated $CuCO_3$, dissolved $Cu(CO_3)_2^{2-}$) was eventually not considered because simulations revealed that only a small quantity of soluble $CuCO_3$ may appear at low dilution (factory effluent) for slurries without complexing agent. $Cu(CO_3)_2^{2-}$ was shown to appear in large quantities at very high pH (above 10) in simulations but the assumption used in the calculation that the solutions are in equilibrium with atmospheric CO2 is unrealistic at such high pH.

Surface complexation, i.e. the adsorption of copper onto silica and alumina particles, will also be considered. Adsorption of metal onto oxide surfaces is the result of a complicated process. Hydroxide groups on the surface of silica (≡Si-OH) or alumina (≡Al-OH) can adsorb metal ions as well as other species such as the solution electrolytes. These groups are commonly modeled as having acid-base reactions such as :

$$\begin{gathered} \equiv Si-OH_2^+ \leftrightarrow H^+ + \equiv Si-OH \\ \equiv Si-OH \leftrightarrow H^+ + \equiv Si-O^- \end{gathered}$$

$$\begin{gathered} \equiv Al-OH_2^+ \leftrightarrow H^+ + \equiv Al-OH \\ \equiv Al-OH \leftrightarrow H^+ + \equiv Al-O^- \end{gathered}$$

Modeling of these reactions should take into account the free energy for bond creation (represented by an intrinsic equilibrium constant) as well as electrostatic effects. The analysis of the surface groups on the surface of silica particles dispersed in CMP slurries has been conducted at the University of Arizona at Tucson (Pr Srini Raghavan, Yuxia Sun) and is presented in [RAGHAVAN 1999] and [SUN 2000] :

$$\begin{aligned} \equiv Si-OH_2^+ \leftrightarrow H^+ + \equiv Si-OH \quad & pKa_1 : N/A \\ \equiv Si-OH \leftrightarrow H^+ + \equiv Si-O^- \quad & pKa_2 = 5.9 \end{aligned}$$

At pH higher than 2~3, the surface of silica particles is negatively charged and will certainly attract Cu^{2+} ions that will then bind to the surface. The equilibrium constants for the formation of surface bonds are from the work at the University of Arizona :

$$\equiv Si-OH + Cu^{2+} \leftrightarrow \equiv Si-OCu^+ + H^+ \quad \log K = -4.35$$

The above constants are intrinsic equilibrium constants and the electrostatic effects are taken into account by a double layer model.

The properties of the silica particles are those of the Degussa Aerosil 90 fumed silica particles, which have a surface area of 90 m^2/g and a density of silanol groups of 2.5 per nm^2. Fumed silica particles are usually used at a point-of-use concentration of 8~15% while colloidal silica particles may have a larger surface area and are used at a point-of-use concentration of 25~30%. These numbers are used to calculate the number of sites available for adsorption at the various stages of the process.

The intrinsic equilibrium constants for the double layer model of adsorption of copper on alumina are [SUN 2000-2] :

$$\equiv Al-OH_2^+ \leftrightarrow H^+ + \equiv Al-OH \quad pKa_1 = 7.2$$

$$\equiv Al-OH \leftrightarrow H^+ + \equiv Al-O^- \quad pKa_2 = 9.5$$

$$\equiv Al-OH + Cu^{2+} \leftrightarrow \equiv H^+ + Al-OCu^+ \quad \log K = -2.1$$

It is not expected that they will contribute significantly to the removal of copper from solution by adsorption at the pH of interest (pH = 3~9 since process pH is about pH= 3 and effluent pH cannot exceed pH= 9). This is due to the fact that alumina particles are positively charged below pH = 8 ~ 9. Additionally, alumina particles used in copper CMP have a diameter of about 200 nm and therefore a surface area per gram much lower than that of silica particles (less than 10 m^2 / g). Finally, in the effluents for all the cases that we have considered expect Case 1, silica particles are about ten times more abundant that alumina particles. All these effects justify neglecting adsorption of copper on alumina particles.

To check this hypothesis, a spent slurry containing only alumina particles (no silica) and no complexing agent is titrated and dissolved copper is measured. The same spent slurry is filtered with a 0.2 micron filter to remove alumina particles, titrated and dissolved copper is measured in the same way. As shown on Figure 3-2, no significant difference is noted between the amount of dissolved copper between the filtered and non-filtered spent slurries, supporting the fact that adsorption of copper on alumina particles is not important in the pH range of interest. A simulation using the MINEQL+ software, using the double layer model, a concentration of 3.3 ppm of copper, 0.3 g/l of alumina particles with surface area of 7 m^2/g and 2 Al-OH sites per nm^2 showed no adsorption of copper on alumina particles.

One point should nonetheless be made. Since it is possible that negatively charged copper complexes adsorb on positively charged alumina particles, checking this point would prove necessary to refine the chemical model.

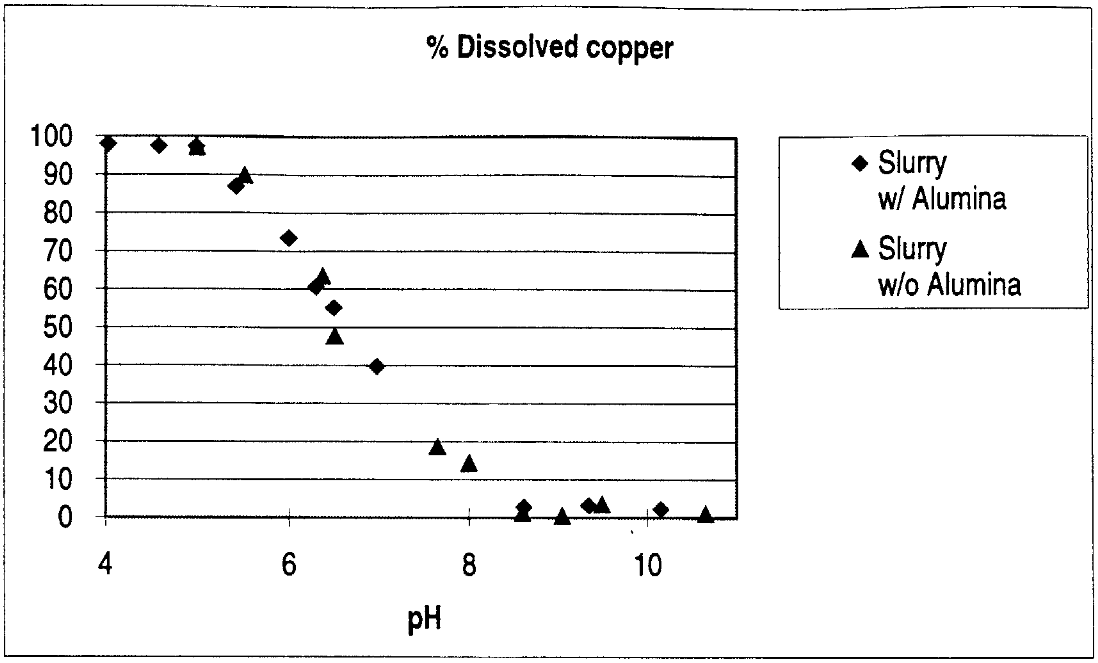


Figure 3-2 : Dissolved copper in a spent slurry with and without alumina particles

3.2. Concentrations at the Nodes of the Facility Effluent Collection System

In Section 2.1.1, the copper content at various nodes of the facility effluent collection system is presented. Since environmental regulations apply to total copper without any concern for its speciation, only these concentrations are shown in Table 2.2 and Figure 2.1.

In order to model copper speciation at the various nodes of the facility effluent collection system, a more precise tracking of the concentration of the chemicals of interest (copper, complexing agents, silica particles) is presented below. Additionally, two types of CMP machines will be modeled : segregated effluent and non-segregated effluent machines. Indeed, either by design or with the addition of a device that sorts process and non-process effluents, some systems have the capability to segregate process effluents from post-CMP clean effluents or process flows from idle flows. In this study, two types of machines will be presented.

The first type of machine has no segregation system so that the polishing process and post-CMP clean effluents as well as idle flows (water flowing while no process is running) are mixed. Such machines are connected to the effluent collection system as follows :

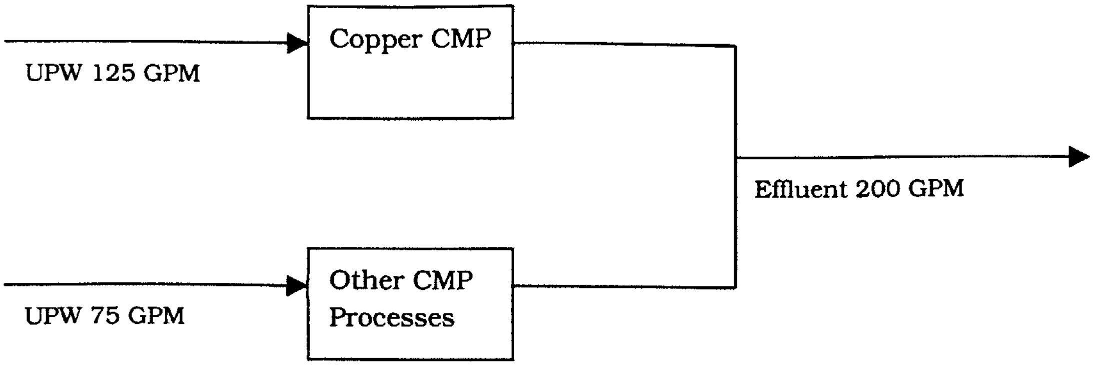


Figure 3-3 : Non-segregated effluent collection system

The second type of machine has a segregation system by design so that polishing process effluents and post-CMP clean effluents are discharged into two different collection systems. Polishing process effluents have a high content of copper, suspended solids and slurry chemicals. Such machines are connected to the effluent collection system as follows :

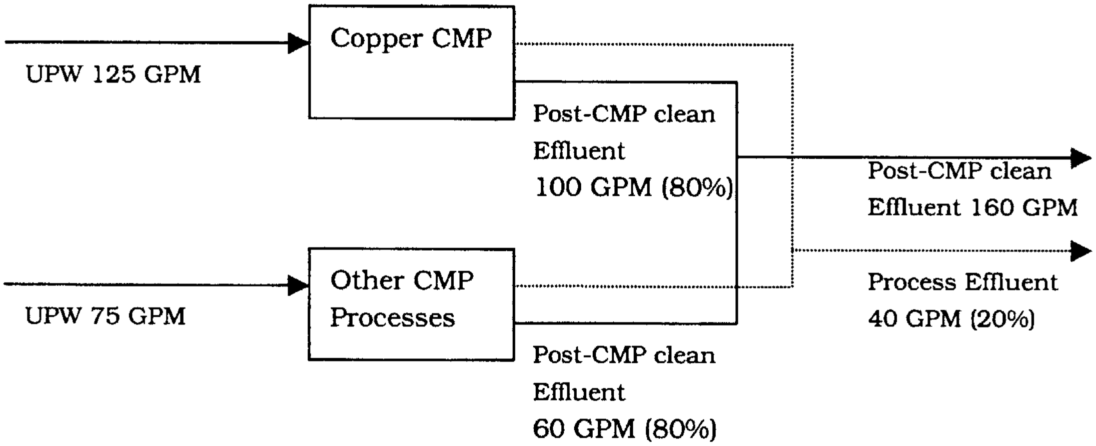


Figure 3-4 : Segregated effluent collection systems

The obvious advantage of such a collection system is that post-CMP clean effluents which are relatively free of suspended solids can easily be handled by the facility existing treatment system. Additionally, the polishing process effluents which have a high content of suspended solids and copper can be efficiently treated in a smaller system since they represent only 20% of the total CMP effluents.

In segregated machines as we have defined them, one effluent collection system is connected to the polishing platens and another is connected to the post-CMP clean sub-unit. In the former, relatively clean idle flows are mixed with highly contaminated polishing process effluents. In this study, only averages are modeled. Peak concentrations can easily be calculated by dividing average concentrations by the machine uptime rate of 60% [see Table 2.1].

The calculation of chemicals concentration is performed in six different cases that basically cover all possible situations in a semiconductor manufacturing facility (Fab). The list of the effluents they contain is shown in Table 3-4 and described in some detail in Table 3-5.

Case	Copper CMP			Other CMP		Total Fab
	Copper Polishing	Ta/TaN Removal	Post-CMP Clean	Polishing Steps	Post-CMP Clean	Other Fab Effluents
1	X					
2	X	X				
3	X	X		X		
4	X	X	X			
5	X	X	X	X	X	
6	X	X	X	X	X	X

Table 3-4 : Effluents modeled in this study

Case	Description
1	Effluent from the copper polish step only Collected from the copper polish platen (not a real-life case) Low pH, high copper content, alumina particles, no silica particles
2	Effluent from the copper polishing and barrier removal steps Segregated effluent from a copper CMP dry-in / dry-out machine High copper content (lower than case 1), alumina and silica particles
3	Mix of all CMP segregated effluents Rather high copper content, alumina and silica particles
4	Non-segregated copper CMP effluents Average copper content, alumina and silica particles
5	Non-segregated CMP effluents (collected from all tools) Average copper content, alumina and silica particles
6	Total facility effluents Rather low copper content, alumina and silica particles

Table 3-5 : Description of the effluents modeled in this study

The mass balance, concentrations and consumables consumption calculations are shown in Table 3-7 and Table 3-8 and summarized in Table 3-6. Details of concentrations in the case of segregated and non-segregated effluent collection systems are shown in Figure 3-5 and Figure 3-6.

The facility generates 1 ton of sludge (dry-weight basis) per day.

CONCENTRATIONS	Case					
	1	2	3	4	5	6
	Copper Polishing Effluents	**Copper CMP Segregated Effluents**	**Total Segregated Effluents**	**Copper CMP Total Effluents**	**CMP Total Effluents**	**Total Plant Effluents**
Cu (ppm)	17.7	8.9	5.5	1.8	1.1	0.26
Alumina (ppm)	1583	792	495	158	99	23
Silica (ppm)	0	3958	3958	792	792	183
Si-OH sites (Meq/l)		1.5E-03	1.5E-03	3.0E-04	3.0E-04	6.8E-05
TSS (ppm)	1583	4749	4453	950	891	206
Cu (mol/l)	2.8E-04	1.4E-04	8.7E-05	2.8E-05	1.7E-05	4.0E-06
Complexing agent (mol/l)	2.8E-04	1.4E-04	8.7E-05	2.8E-05	1.7E-05	4.0E-06

Table 3-6 : Concentrations at various stages of effluent collection

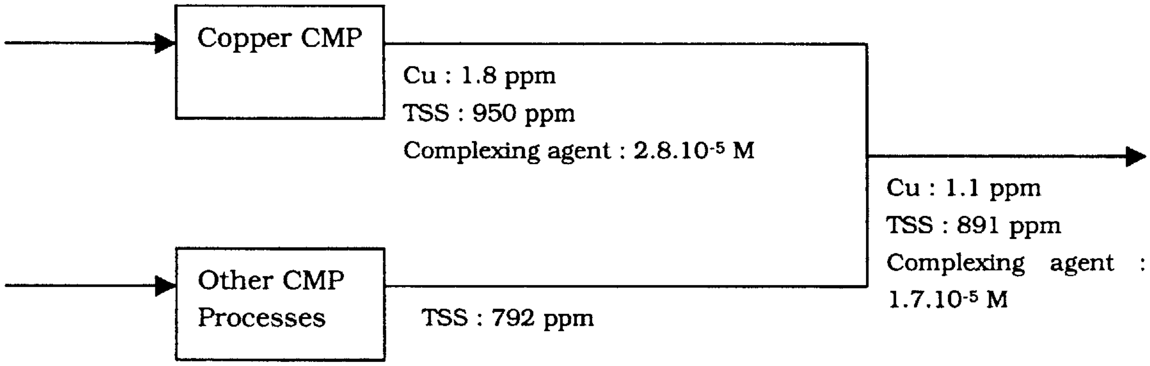


Figure 3-5 : Concentrations in a non-segregated effluent collection system

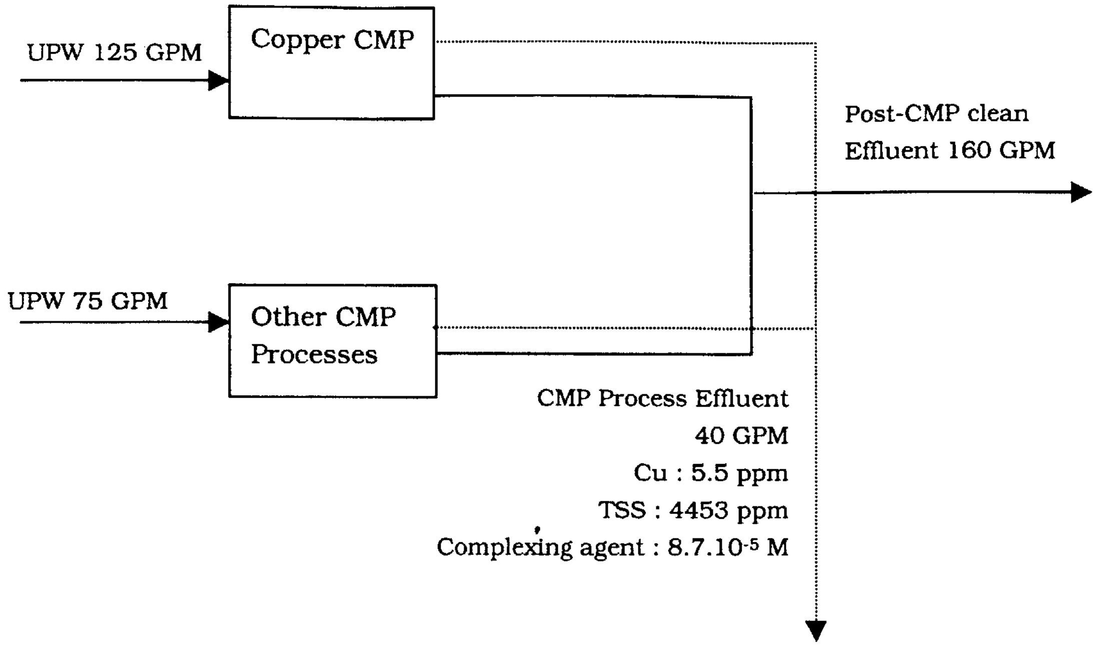


Figure 3-6 : Concentrations in a segregated effluent collection system

	Copper CMP			Other CMP		Copper CMP Polishing effluents	Copper CMP Segregated effluents	Total Segregated Effluents	Copper CMP CMP + clean	Other CMP CMP + rinse	Total CMP Effluents
	Cu Polishing B	Ta polishing C	Clean D	Polishing E	Clean F	B	B + C	B + C + E	B + C + D	E + F	B + C + D + E + F
Number of steps	5	5	5	3	3						
PER STEP											
Gallons of water	2.5	2.5	20.0	5.0	20.0						
Idle flow (40% of the time) (Gallon	1.7	1.7	13.3	3.3	13.3						
Liters of water	9.5	9.5	75.8	19.0	75.8						
Idle flow (40% of the time) (liters)	6.3	6.3	50.5	12.6	50.5						
Slurry flow (l)	0.5	0.5		0.5							
Cu (mg)	280										
Alumina (5% in slurry) (ppm)	50000										
Alumina used (mg)	25000										
Silica (25% in slurry) (ppm)		250000		250000							
Silica used (mg)		125000		125000							
Complexing agent used (mol)	4.4E-03										
PER WAFER											
Total water (Gallons)	20.8	20.8	166.7	25.0	100.0	20.8	41.7	66.7	208.3	125.0	333.3
Total Water (l)	79.0	79.0	631.7	94.8	379.0	79.0	157.9	252.7	789.6	473.8	1263.3
Total Cu (mg)	1400	0	0	0	0	1400	1400	1400	1400	0	1400
Total Alumina (mg)	125000	0	0	0	0	125000	125000	125000	125000	0	125000
Total Silica (mg)	0	625000	0	375000	0	0	625000	1000000	625000	375000	1000000
Total TSS (mg)	125000	625000	0	375000	0	125000	750000	1125000	750000	375000	1125000
Total Complexing agent (mol)	2.2E-02					2.2E-02	2.2E-02	2.2E-02	2.2E-02		2.2E-02

Table 3-7 : Mass balance of chemicals in the model factory

CONCENTRATIONS	**Case**						
	1	**2**	**3**	**4**		**5**	**6**
	Copper Polishing Effluents	**Copper CMP Segregated Effluents**	**Total Segregated Effluents**	**Copper CMP Total Effluents**	**Other CMP Polishing + Clean**	**CMP Total Effluents**	**Total Plant Effluents**
Cu (ppm)	17.7	8.9	5.5	1.8	0.0	1.1	0.26
Alumina (ppm)	1583	792	495	158	0	99	23
Silica (ppm)	0	3958	3958	792	792	792	183
Si-OH sites (Meq/l)		1.5E-03	1.5E-03	3.0E-04	3.0E-04	3.0E-04	6.8E-05
TSS (ppm)	1583	4749	4453	950	792	891	206
Cu (mol/l)	2.8E-04	1.4E-04	8.7E-05	2.8E-05		1.7E-05	4.0E-06
Complexing agent (mol/l)	2.8E-04	1.4E-04	8.7E-05	2.8E-05		1.7E-05	4.0E-06

MASS PER DAY (900 wafers per day)		
Total water (Gallons)	300000	1296000
Total water (liters)	1137000	4911840
Cu (Kg)	1.26	1.26
Alumina (Kg)	112.5	112.5
Silica (Kg)	900	900
Sludge (TSS) (kg)	1012.5	1012.5

Table 3-8: Concentrations at various stages of the process and total consumable consumption

3.3. Copper Speciation at the Various Stages of the Process

Simulations were run with the MINEQL+ software for the three types of slurries described in Section 3.1.1 and the six cases defined in Table 3-4. Simulation results are presented in Figure 3-9, and Figure 3-11. Assuming that the components that are included in the chemical model accurately determine copper speciation, the fate of copper in the effluent collection system can be determined from these figures, provided that pH is known.

Slurry Type A (no complexing agent) - Figure 3-9

The effluent of the copper polishing stage (case 1) has a low pH and contains no silica particles. Copper is completely dissolved in the Cu^{2+} form. This effluent is usually not segregated in the CMP tool.

In all other cases, the only two species that may be present at a pH below 9 are Cu^{2+} and $\equiv Si\text{-}OCu^{+}$ (copper adsorbed onto silica particles). The partition between the two species is strongly dependent on pH. In all cases, adsorbed copper appears at pH around 5 ~ 6 and represents 100% of the copper at pH 7 and above as shown in Figure 3-7.

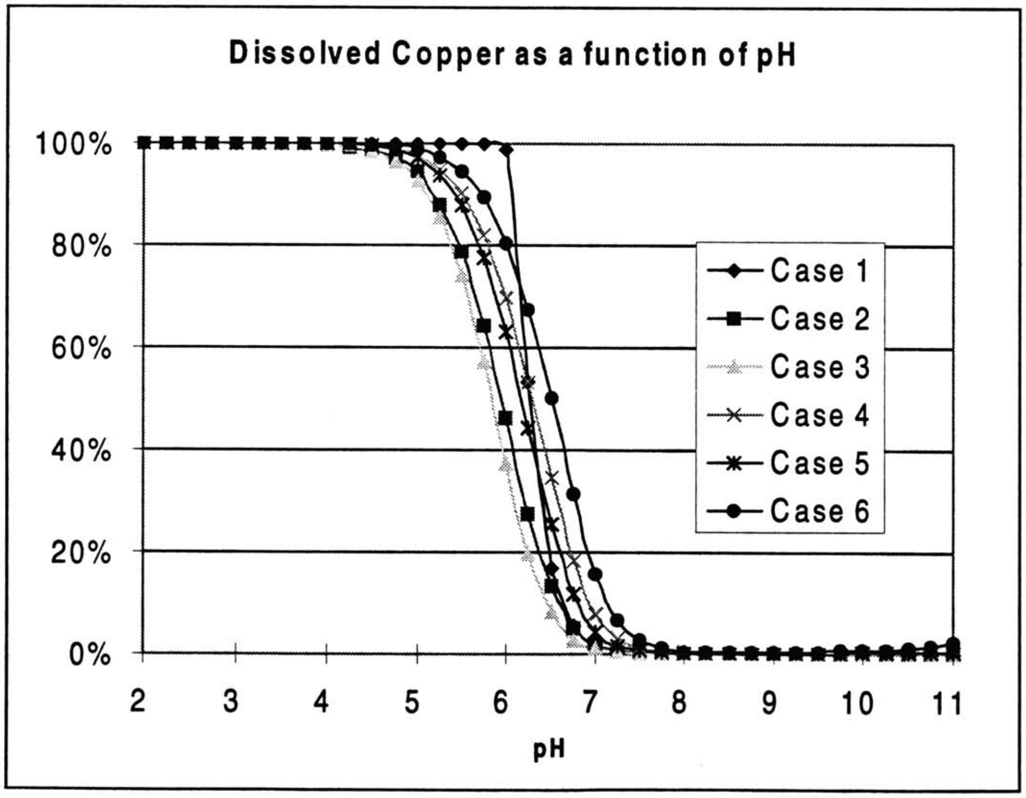


Figure 3-7 : Dissolved copper as a function of pH at various nodes of the effluent collection system (Slurry Type A)

Slurry Type B (Citrate as complexing agent) -

The effluent of the copper polishing stage (case 1) has a low pH and contains no silica particles. Copper is completely dissolved in the Cu^{2+} and $Cu:Cit^-$ forms. $Cu:Cit^-$ appears at pH above 3.

In all other cases, the presence of citrate decreases the adsorption on silica particles and copper remains completely dissolved at pH up to 5.5 ~ 6. Above pH 6, $\equiv Si\text{-}OCu^+$ starts to appear but never exceeds 40% of total copper at pH 7. $Cu(OH)_{2.s}$ precipitate does not appear before pH 8.5 ~ 9.5.

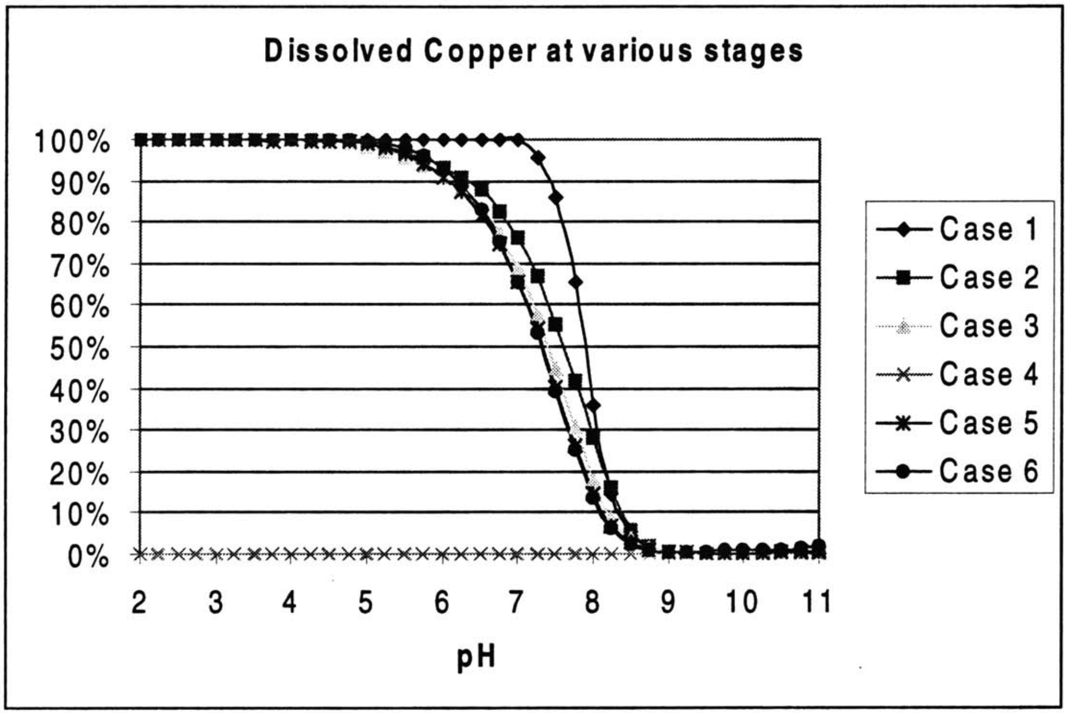
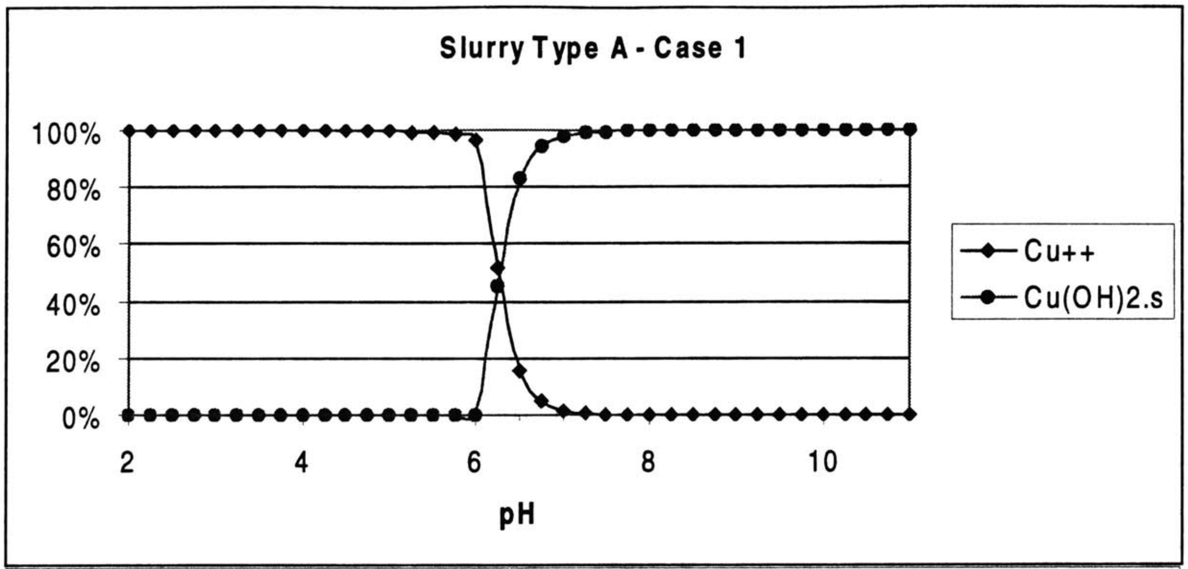
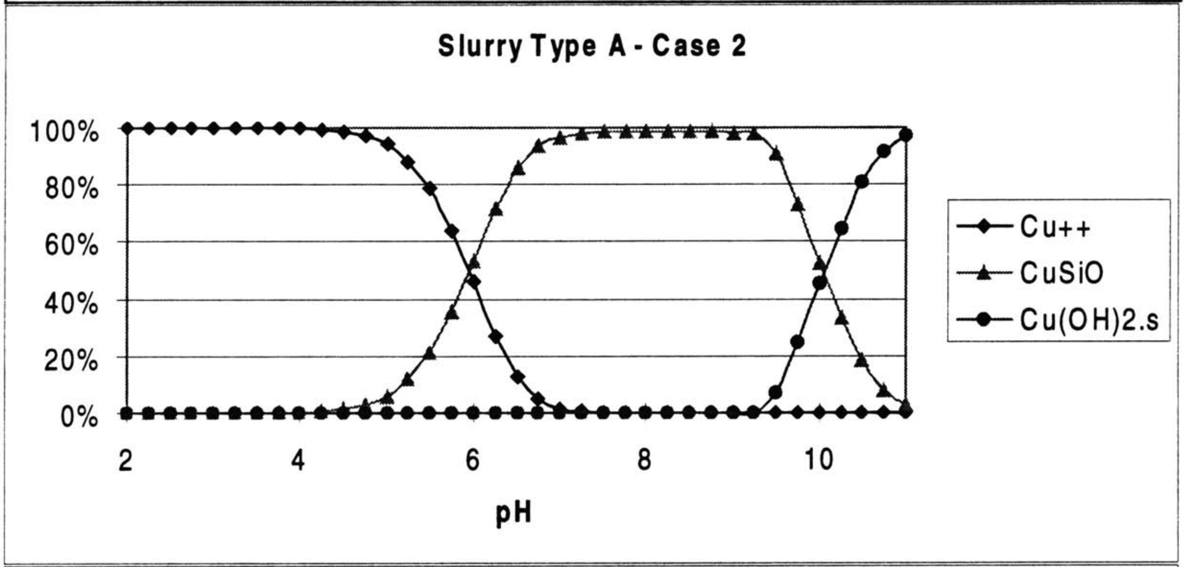


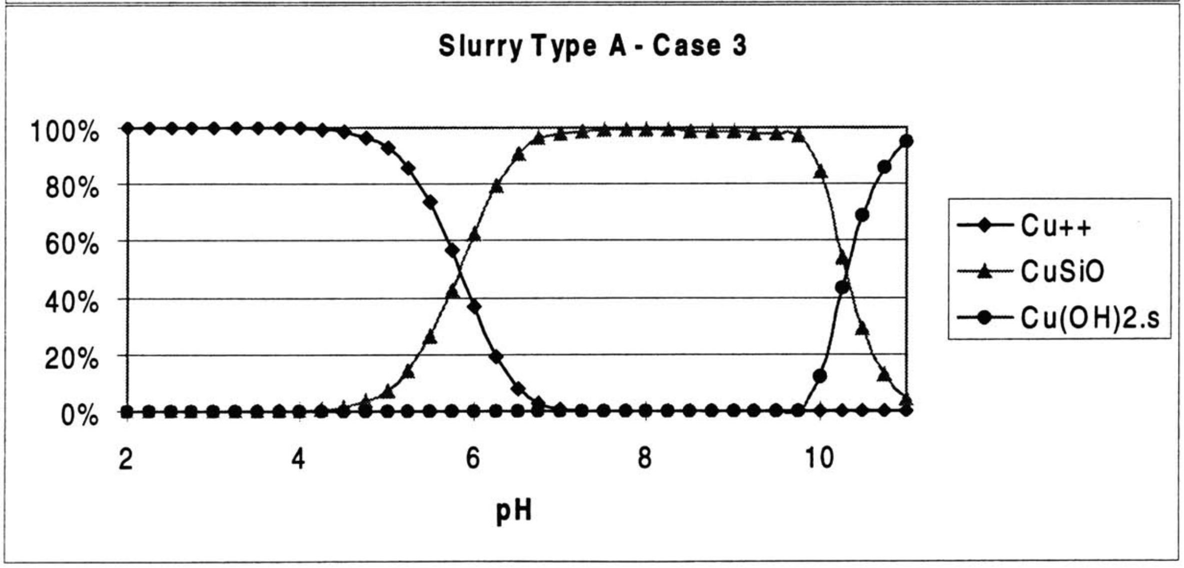
Figure 3-8 : Dissolved copper as a function of pH at various nodes of the effluent collection system (Slurry Type B)

Slurry Type C (EDTA as complexing agent) - Figure 3-9

In all cases, adsorption on silica particles is completely inhibited. Copper is dissolved at all pH values in Cu^{2+}, $Cu:EDTA^{2-}$ or $CuOH:EDTA^{3-}$ forms.


Slurry Type A - Case 1


Slurry Type A - Case 2


Slurry Type A - Case 3

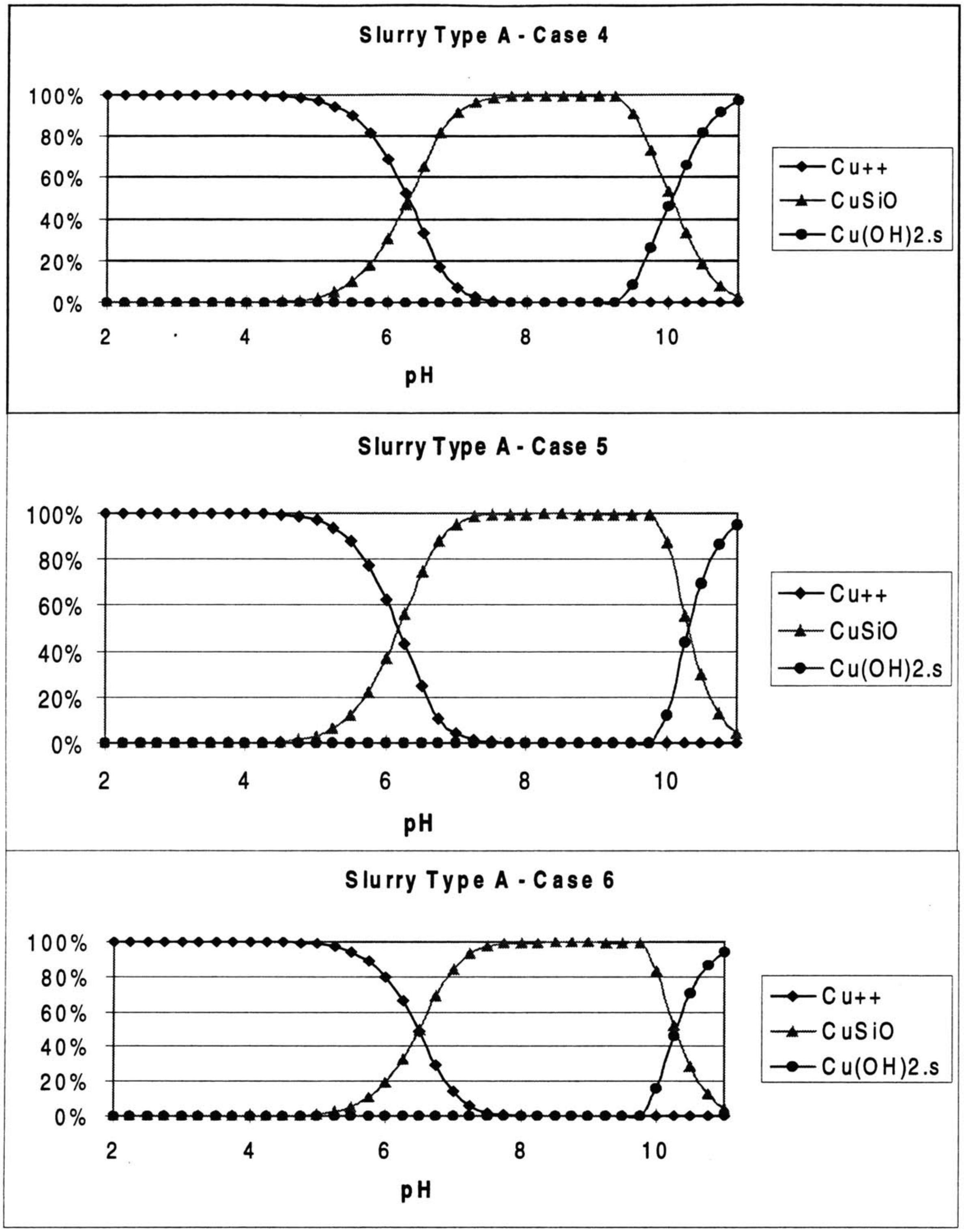
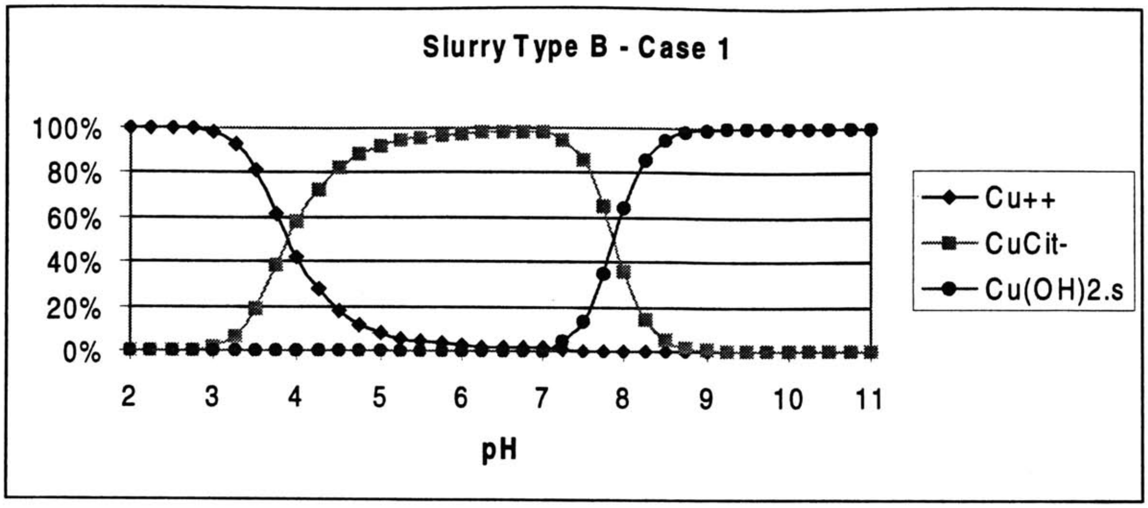
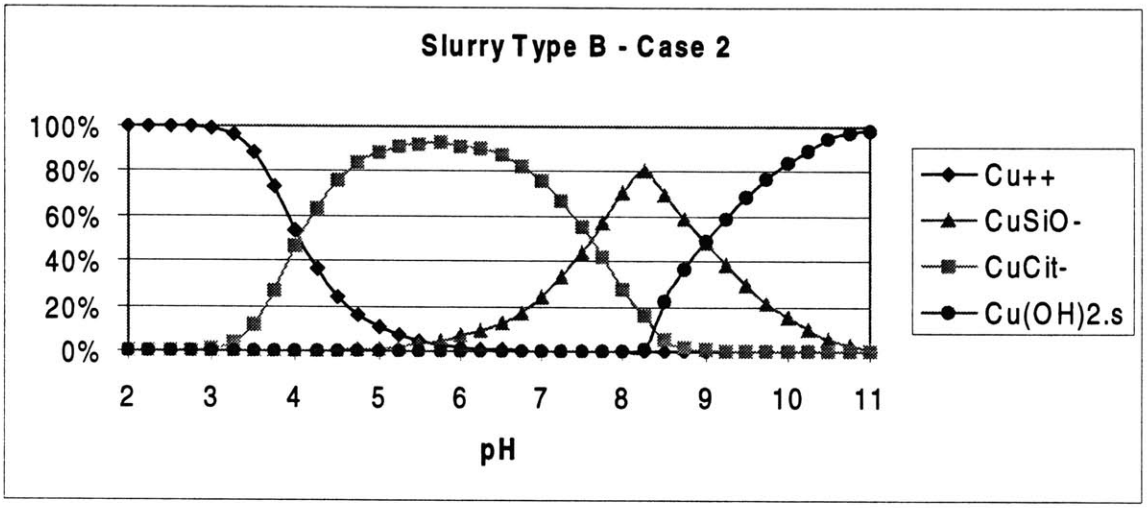
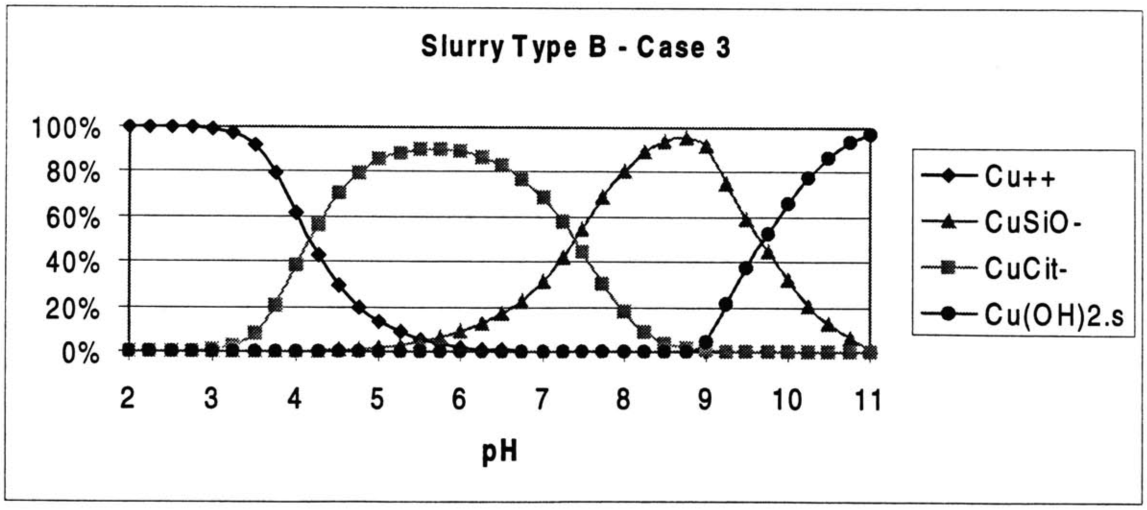
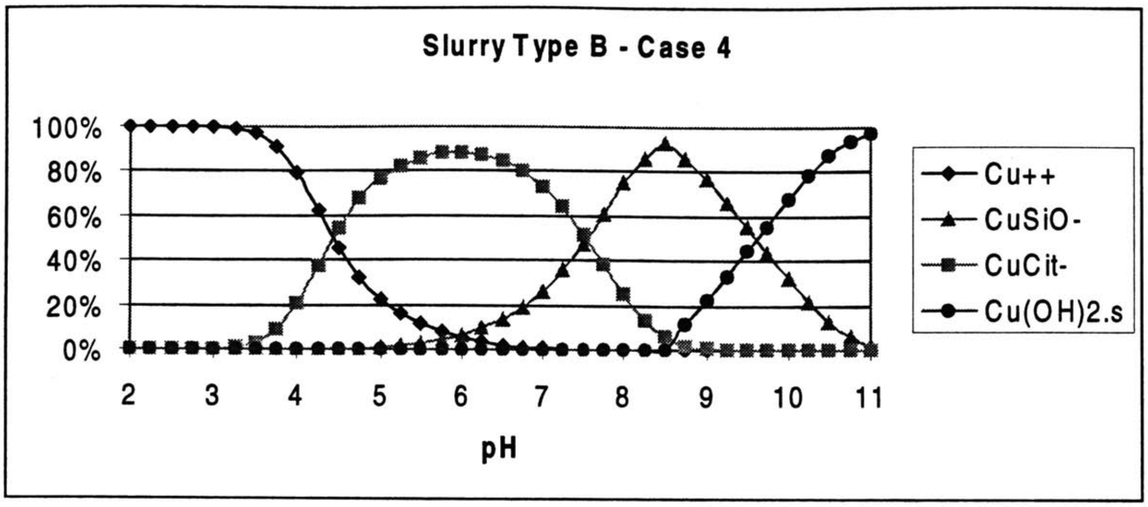


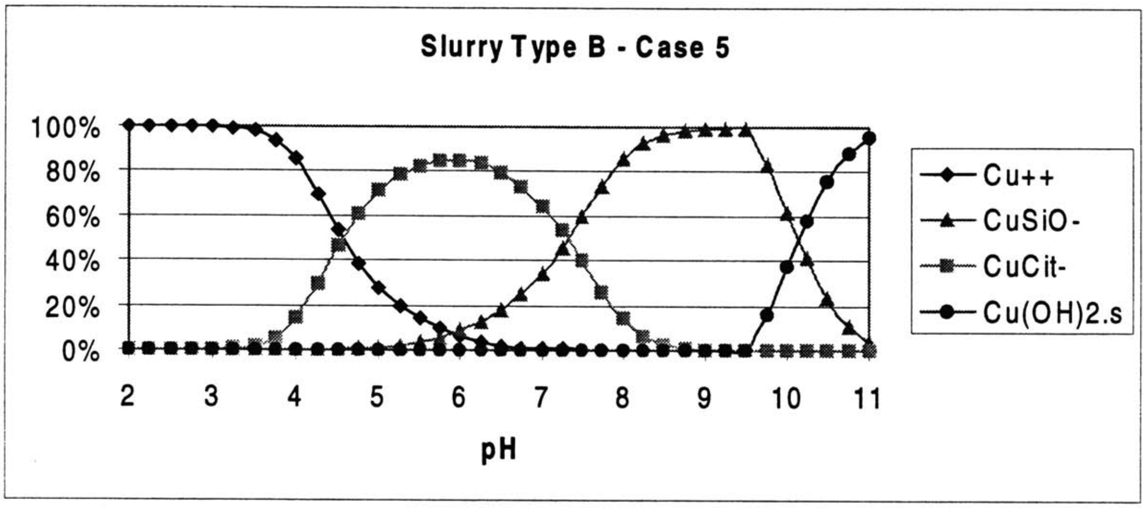
Figure 3-9 : Simulation of the speciation of Slurry Type A (no complexing agent)


Slurry Type B - Case 1
100%
80%
60%
40%
20%
0%
2
3
4
5
6
7
8
9
10
11
pH
Cu++
CuCit-
Cu(OH)2.s


Slurry Type B - Case 2
100%
80%
60%
40%
20%
0%
2
3
4
5
6
7
8
9
10
11
pH
Cu++
CuSiO-
CuCit-
Cu(OH)2.s


Slurry Type B - Case 3
100%
80%
60%
40%
20%
0%
2
3
4
5
6
7
8
9
10
11
pH
Cu++
CuSiO-
CuCit-
Cu(OH)2.s





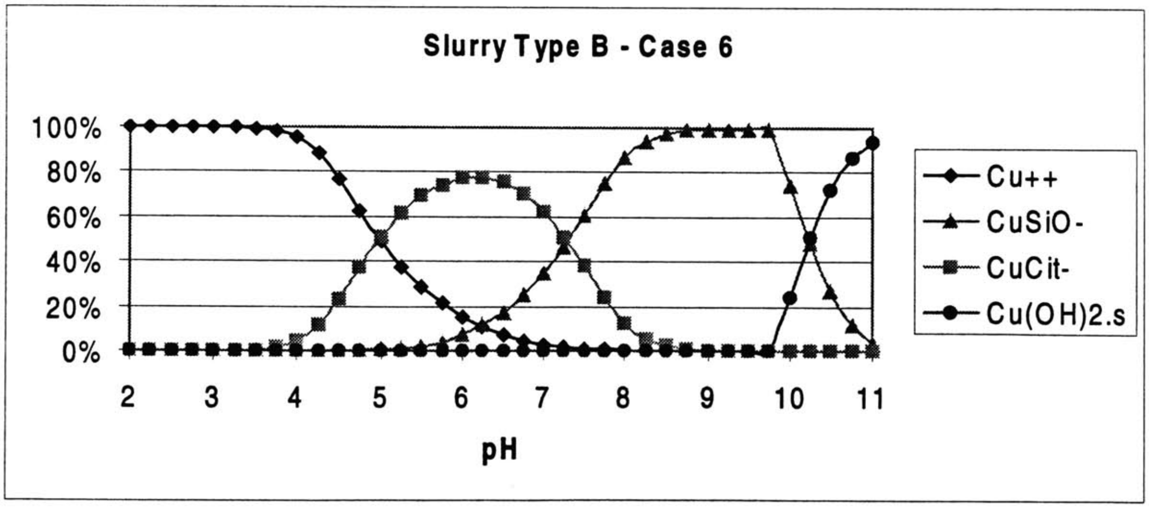
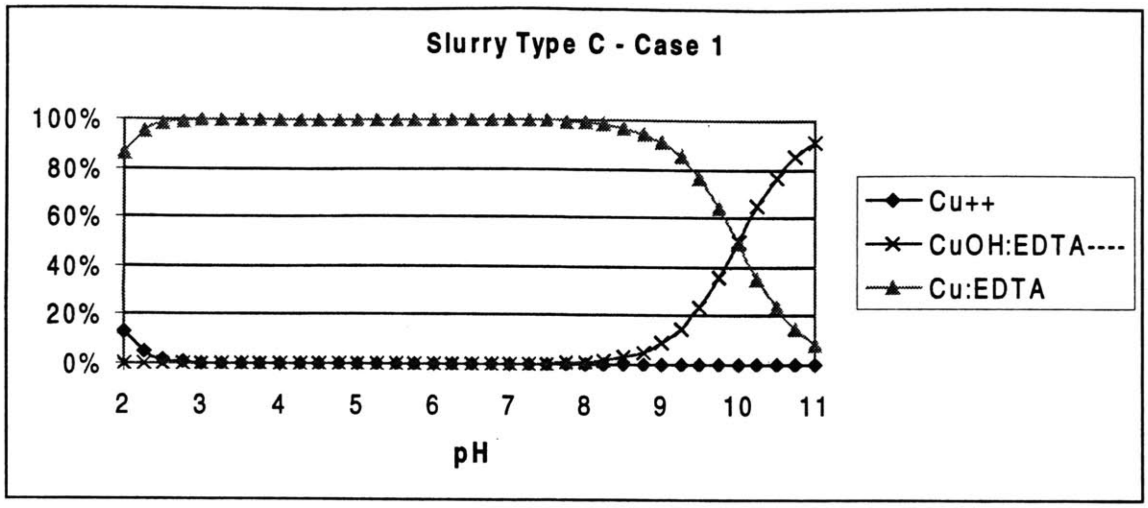
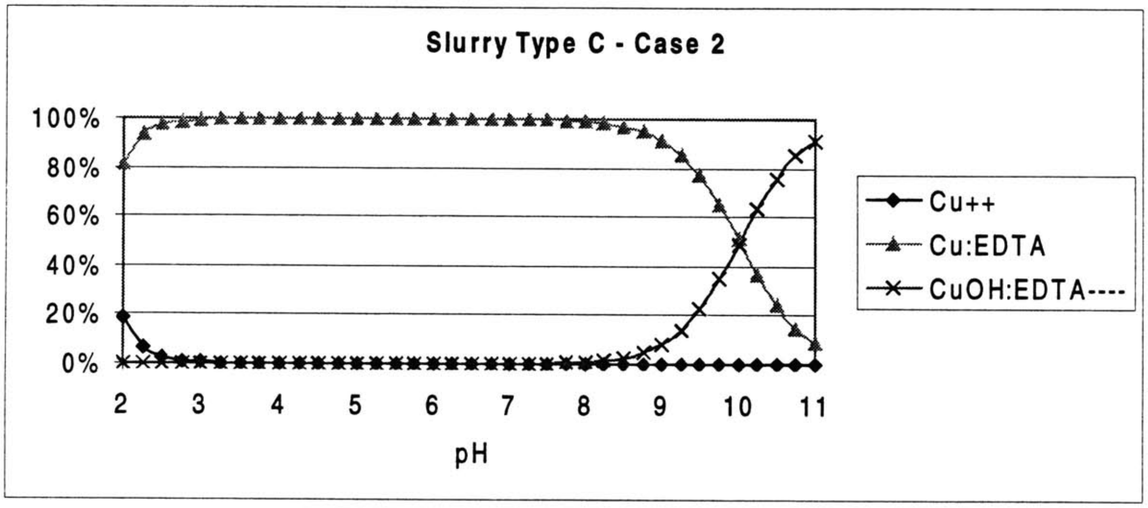
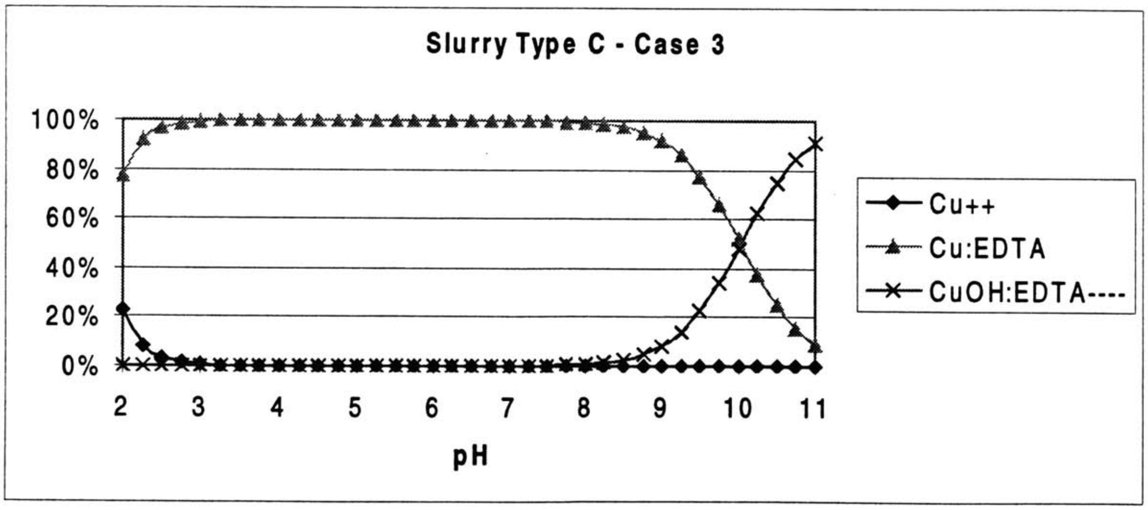
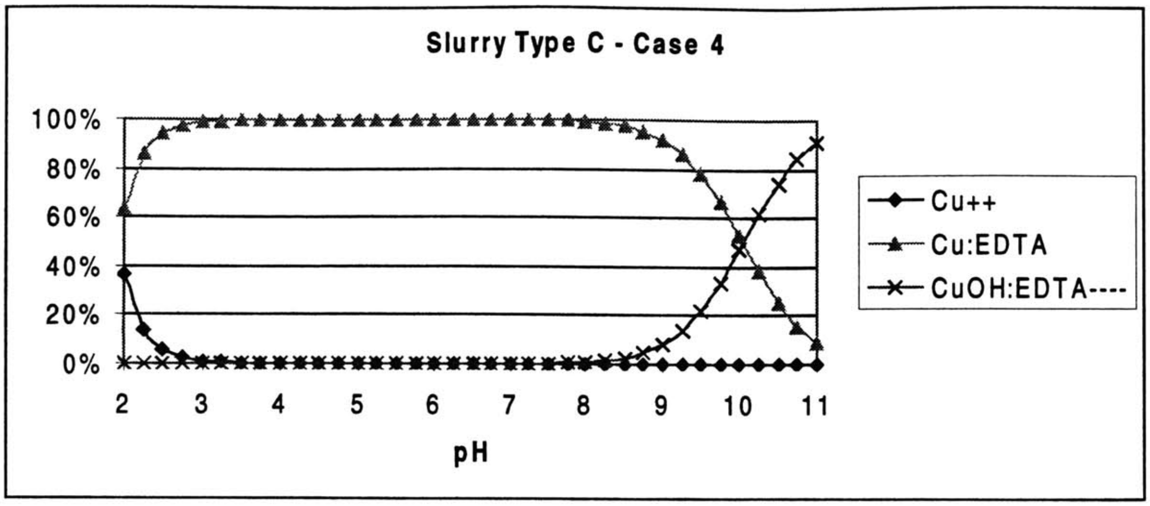


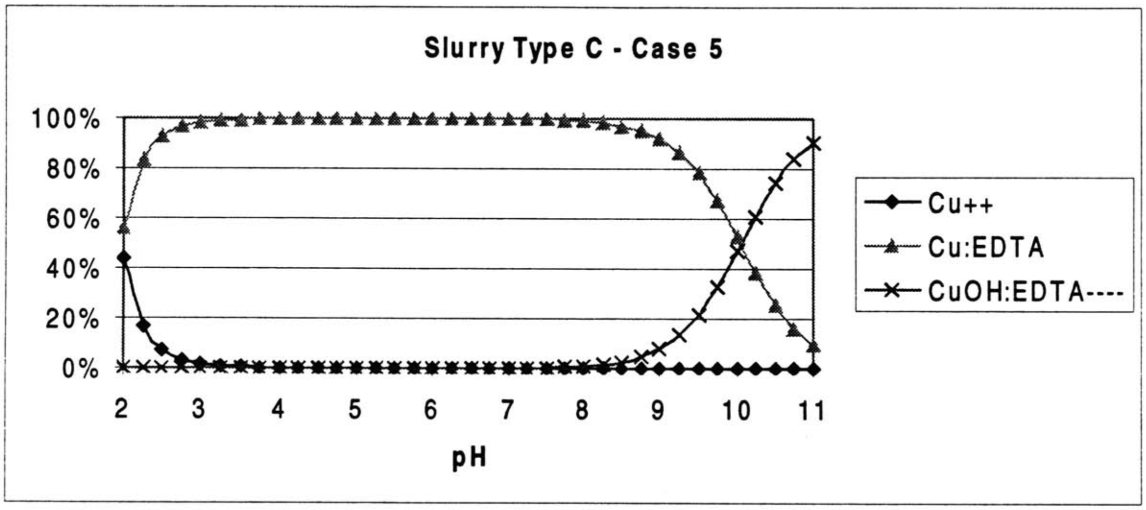
Figure 3-10 : Simulation of the speciation of Slurry Type B (Citrate as complexing agent)


Slurry Type C - Case 1
100%
80%
60%
40%
20%
0%
2
3
4
5
6
7
8
9
10
11
pH
Cu++
CuOH:EDTA----
Cu:EDTA


Slurry Type C - Case 2
100%
80%
60%
40%
20%
0%
2
3
4
5
6
7
8
9
10
11
pH
Cu++
Cu:EDTA
CuOH:EDTA----


Slurry Type C - Case 3
100%
80%
60%
40%
20%
0%
2
3
4
5
6
7
8
9
10
11
pH
Cu++
Cu:EDTA
CuOH:EDTA----





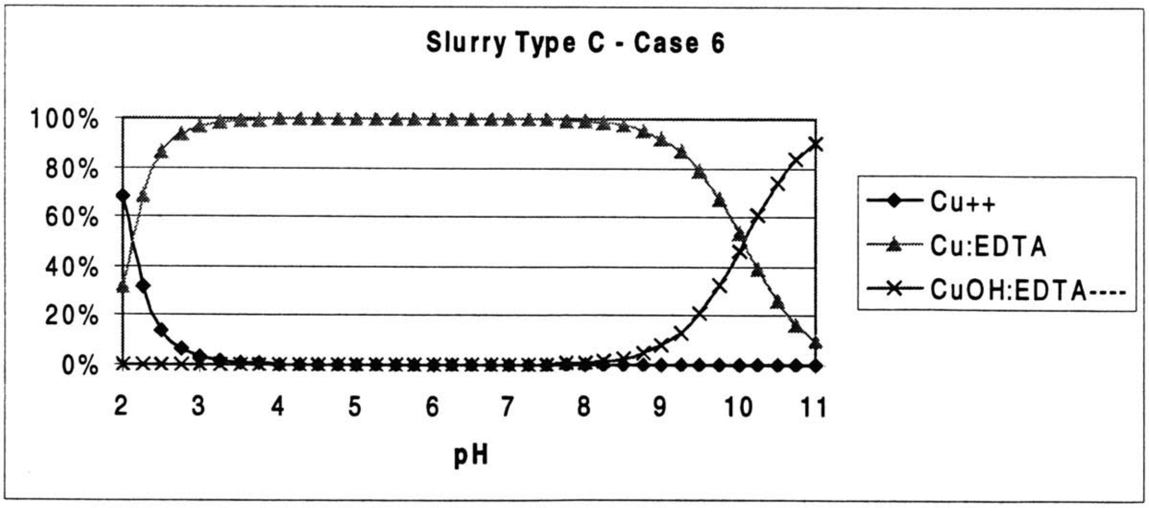


Figure 3-11 : Simulation of the speciation of Slurry Type C (EDTA as complexing agent)

Simulations are run assuming that there is a molar equivalence between copper and the complexing agent. If the amount of complexing agent is lower (for example if it decays quickly), adsorption on silica particles will be modified. To illustrate this point, the copper speciation for Case 3 with a citrate-deficient or an EDTA-deficient slurry (7.10^{-5} M of Citrate or EDTA for a concentration of copper of $8.7.10^{-5}$ M) is shown in Figure 3-12 and Figure 3-13 respectively.

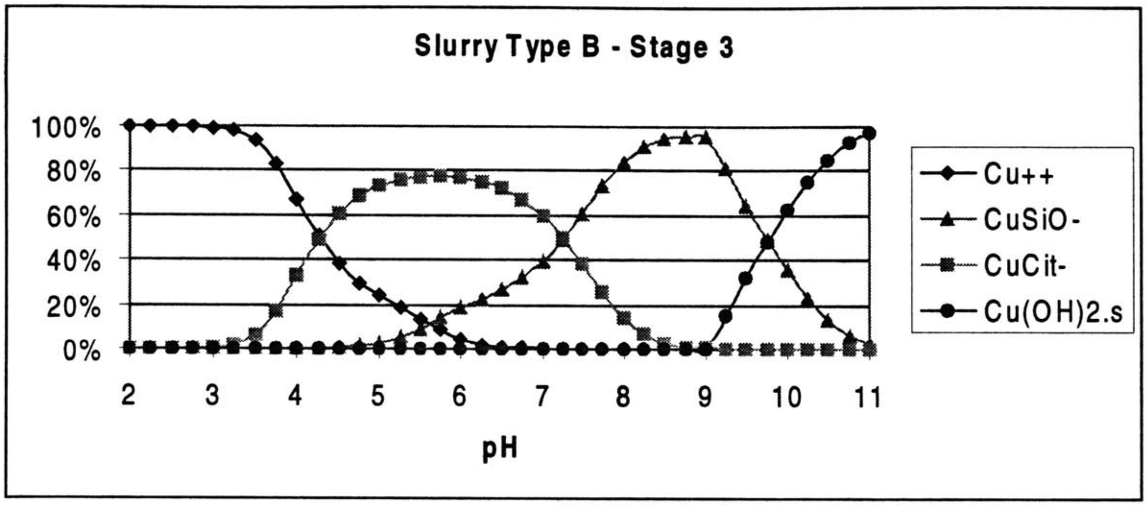


Figure 3-12 : Copper speciation in a Citrate-deficient slurry. The effect of Citrate deficiency is the increased adsorption on silica particles.

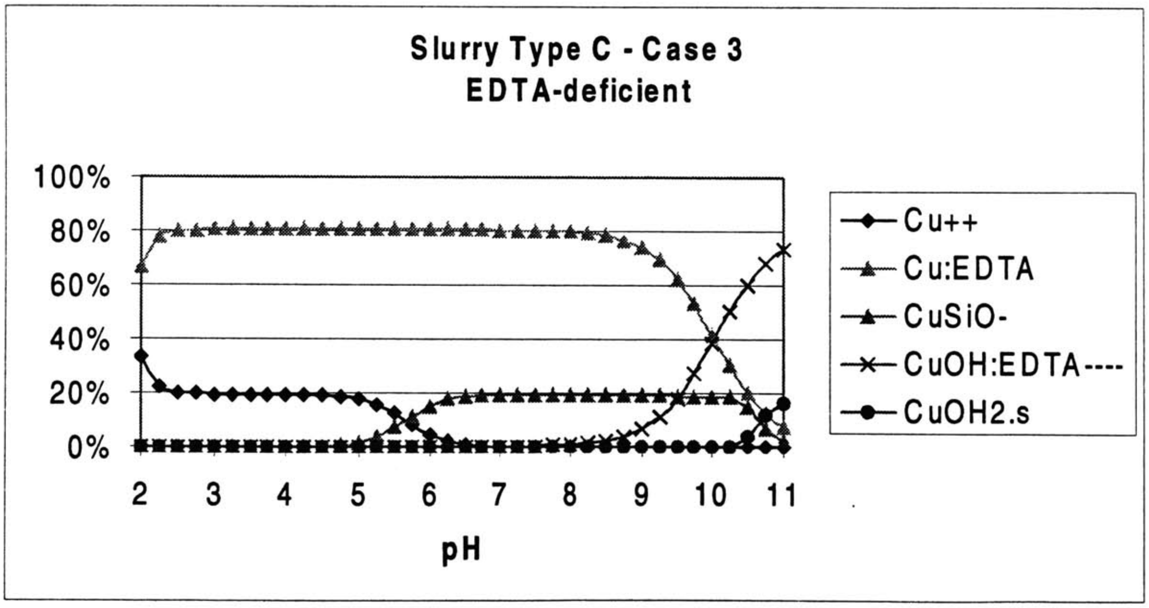


Figure 3-13 : Copper speciation in an EDTA deficient slurry. The effect of EDTA deficiency is the appearance of ≡Si-OCu+, which was completely inhibited in an EDTA-rich slurry.

3.4. Experimental Work

3.4.1. Experimental Method

The purpose of the experiments is to determine the speciation of copper in typical process effluents (if such a typical effluent can actually be defined) and to see whether mixing with wastewater would change copper speciation.

In order to separate dissolved copper from particulate copper, syringe filters of size 0.8 µm, 0.45 µm, 0.2 µm (Pall Gelman Acrodisk filters # 4188, #4184 and #4182 respectively) and 0.02 µm (Whatman Anatop 25 sterile) are used (see Figure 3-14).

Figure 3-14 : Filtering equipment

Copper contents are measured with the Perkin Elmer 360 flame atomic adsorption spectrophotometer shown in Figure 3-15. In that apparatus, solutions are pumped through an air-acetylene flame where copper is atomized. Light from a lamp at 324.7 nm is passed through the flame and collected on the other side. The amount of light at 324.7 nm absorbed is proportional to the copper content. The apparatus gives a linear response up to 6 ppm and has a precision around 0.1 - 0.2 ppm. Before measurement, solutions are acidified with nitric acid 16 M so as to reach a concentration of 1% of acid in the solution. When solutions containing suspended particles are measured, particles are given time to settle and the supernatant is pumped through the atomic absorption spectrophotometer.

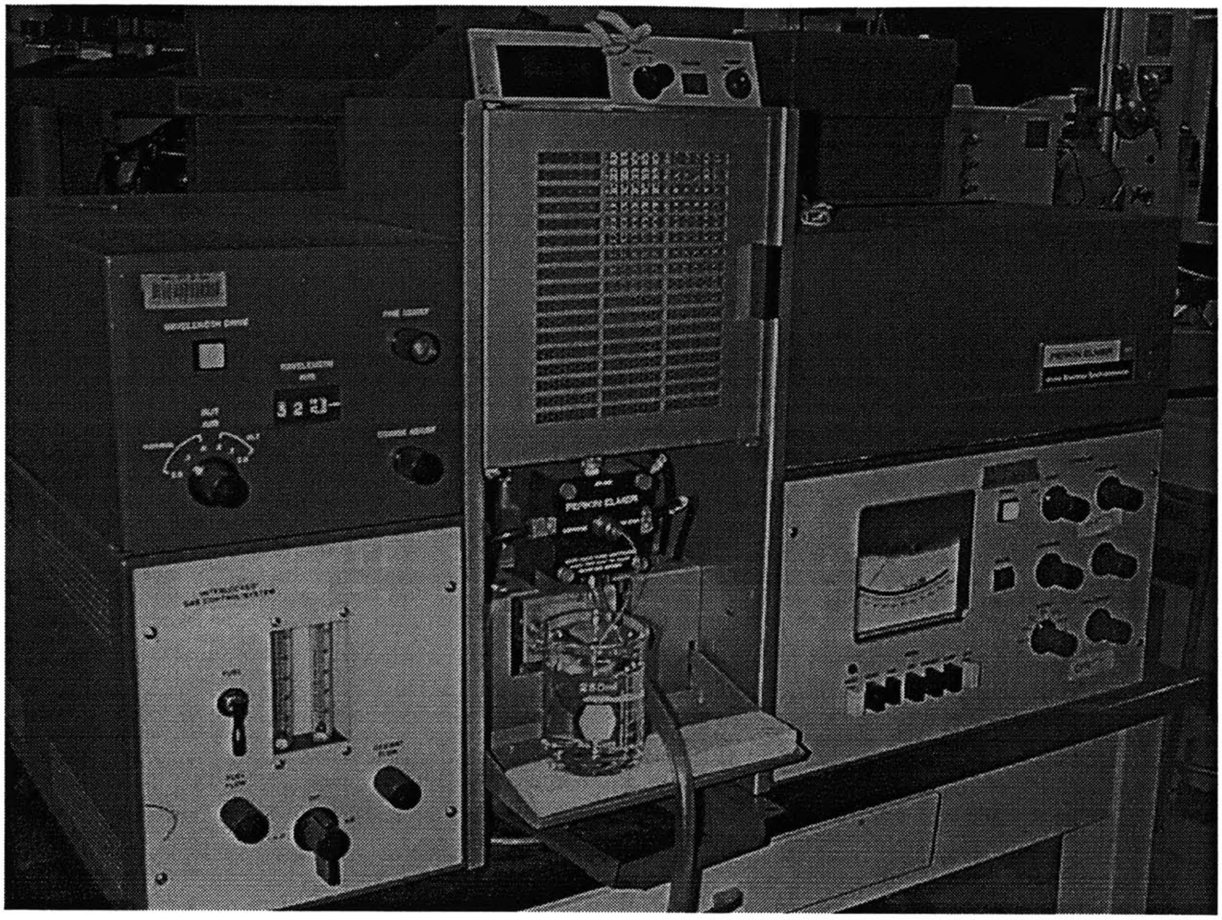


Figure 3-15 : Flame atomic absorption spectrophotometer

In order to determine the proportion of soluble copper that is strongly complexed, solutions are passed through a chelating resin column (Biorad Chelex 100 resin – see Figure 3-16), following the method described in [SEDLAK 1997]. The resin has an amino dicarboxylate chelating functional group with a density of 0.4 meq/ml and will bind to weakly complexed copper or free copper ions while strongly complexed copper will go through. Tests show that both citrate and EDTA complexed copper will go through the Chelex 100 resin column. In this study, strongly complexed copper is operationally defined as copper that passes through the Chelex-100 resin column, and weakly complexed copper as copper that does not.

Figure 3-16 : Chelex resin columns

3.4.2. Experimental Results

Experiments are conducted on three process effluents, which are referred to as Sample (1), Sample (2) and Sample (3). These samples were generously supplied by several manufacturers. Sample (1) and Sample (3) come from the same manufacturer. Wastewater samples were kindly provided by the Massachusetts Water Resources Authority.

All samples have an opaque appearance but suspended particles in samples (1) and (3) did not settle significantly after 2 weeks of storage while those in sample (2) settled in a matter of hours. Visible particles are removed from sample (1) by a 0.45 µm filter while they are removed from samples (2) and (3) with a 0.8 µm filter (see Table 3.10).

Sample (1) and Sample (3) are segregated CMP effluents containing waste from copper CMP as well as other CMP tools (Case 3). Sample (2) is an effluent from the first step of the copper CMP process and contains only alumina particles. It does not include idle flows however, so it cannot be modeled by Case 1, but rather by a 'Case 0' whose composition is that of Case 1 divided by the machine uptime ratio of 60%.

The predicted composition of these samples from the facility model as well as the measured copper are listed in Table 3-9. Measured copper content of all samples approximately match the values predicted by the facility model, which is a confirmation that facility flows were appropriately taken into account, at least for the CMP part of the process.

	Predicted composition from the facility model		
	Sample (1)	Sample (2)	Sample (3)
Copper	5.5 ppm	29.5 ppm	5.5 ppm
Alumina	495 ppm	2640 ppm	495 ppm
Silica	3958 ppm	0 ppm	3958 ppm
Complexing agent (if any)	$8.7.10^{-5}$ M	$4.7.10^{-4}$ M	$8.7.10^{-5}$ M
	Measured		
Copper	6.2 ppm	26.5 ppm	7.8 ppm

Table 3-9 : Predicted composition from the facility model of the tested samples

The next set of experiments consists in checking whether the chemical model could accurately predict copper speciation.

The experimental results for Sample (1) are presented in Table 3-10. For reference, Sample (1) was collected on February 23rd 2000. Its pH remained constant at 7.1.

	Measured March 7th 2000		Measured March 20th 2000	
Sample	Before Chelex	After Chelex	Before Chelex	After Chelex
Raw sample	6.2 ppm			
0.8 μm filtrate	4.8 ppm			
0.45 μm filtrate	2.4 ppm	0.78 ppm	2.57 ppm	0.31 ppm
0.2 μm filtrate	2.7 ppm	0.95 ppm		
0.02 μm filtrate	3.1 ppm	0.87 ppm		

Table 3-10 : Copper speciation experimental results - Sample (1)

Table 3-10 shows that only about 15% of the total copper is strongly complexed on March 7th (13 days after collection) and 5% on March 20th (26 days after collection). The decrease in copper content can be attributed to either a degradation of the complexing agent (by non-reacted oxidizer from the slurry or biodegradation) or an exchange of the complexing agent between copper and another metal (Tungsten, Tantalum, Silicon). Tungsten is the only one in sufficient quantity to explain this exchange but it is unlikely that it would replace copper in a metal – complexing agent bond because it is strongly hydrolyzed.

Copper speciation in Sample (2) is measured after dilution in DI water (one volume of sample for six volumes of DI water) because its high copper content could not be measured directly. The original pH of the sample (pH = 3.5) was increased through this operation to pH = 4.1. All copper was found to be dissolved in the diluted sample so it is expected that copper was also entirely dissolved in the non-diluted sample at a lower pH (there are no silica particles in this sample and precipitates such as $Cu(OH)_{2,s}$ appear only at pH at least above 6).

Since Chelex resin cannot be accurately used at pH = 3.5, a dilution of one volume of Sample (2) in four volumes of DI water is neutralized to pH = 6.9 with sodium hydroxide and passed through a Chelex resin column. Results show the absence of a strong complexing agent.

A titration of Sample (2) is also performed to expand the range of data needed for the validation of the model. 120 ml of a dilution of one volume of Sample (2) in six volumes of DI water is stirred continuously in a Beaker and titrated with sodium hydroxide 0.03 M. Sodium hydroxide is added about 1 ml at a time and samples are taken from a syringe only one pH has stabilized, which may take a couple of minutes. Raw samples and 0.45 µm filtrates are tested for copper. The experimental results of the titration of Sample (2) along with a prediction based on the total amount of copper measured in Sample (2) are shown in Figure 3-18.

The experimental results for Sample (3) are presented in Table 3-11. For reference, Sample (3) was collected on March 31st 2000. Its pH remained constant at 6.5.

	Measured Apr 3rd		Measured Apr 4th		Measured Apr 10th		Measured Apr 18th	
	Before Chelex	After Chelex	Before Chelex	After Chelex	Before Chelex	After Chelex	Before Chelex	After Chelex
Raw Sample	7.8 ppm		7.8 ppm					
0.8 µm filtrate	7.5 ppm	2.6 ppm	5.2 ppm	1.8 ppm	5.0 ppm	1.5 ppm	5.5 ppm	1.1 ppm
0.45 µm filtrate	8.1 ppm	2.7 ppm						
0.2 µm filtrate	6.6 ppm	2.5 ppm						
0.02 µm filtrate	7.0 ppm	2.8 ppm						

Table 3-11 : Copper speciation experimental results – Sample (3)

The above data suggest, similarly to Sample (1), a decay or bond exchange of the strong complexing agent, signifying that the characteristics of the spent slurry evolve within a few days of its generation as shown in Figure 3-17. Decay is fast at first, then stabilizes. This could be due to the exhaustion of the reagent that degrades the complexing agent (in case of decay), or to the reduced biological activity due to the storage of the samples in a refrigerator after reception (in case of biological decay). At the same time, it seems that copper starts to bind to particulates.

Extrapolating back the strongly complexed copper content to the collection day by using a first-order decay law gives 97% of the copper strongly bound. That is compatible with the hypothesis that the complexing agent content of the slurry at point-of-use is present at the same concentration as copper (on a molar basis) and that the non-reacted oxidizer, present in the slurry in large quantities, degrades the complexing agent according to a pseudo first-order decay law.

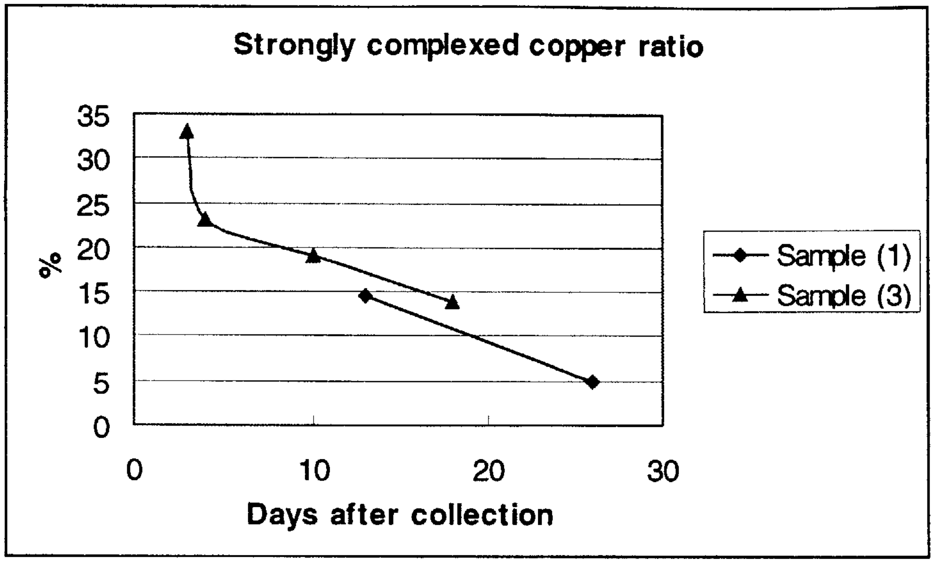


Figure 3-17 : Decay of the strongly complexed copper ratio in samples (1) and (3)

A titration of Sample (3) is performed similarly to the titration of sample (2). Results are presented in Figure 3-22 along with dissolved copper content prediction from the chemical model.

The last set of experiments consists in mixing the samples with wastewater in order to determine whether copper speciation changes with the contact with wastewater. The results are presented in Table 3-12.

	Raw sample	0.45 µm filtrate		0.45 µm filtrate After Chelex
	Measured March 14th 2000			
Sample (1)	6.2 ppm (1)	2.4 ~ 3.1 ppm (1)		0.53 ppm (2)
Sample (1) – Wastewater 1:1 mix	3.1 ppm	1.5 ppm (1.2 ~ 1.6 ppm)		0.19 ppm (0.29 ppm)
Sample (1) – Wastewater 1:2 mix	2.0 ppm	1.0 ppm (0.8 ~ 1.0 ppm)		0.14 ppm (0.21 ppm)
Sample (1) – Wastewater 1:10 mix	0.58 ppm	0.35 ppm (0.27 ~ 0.33 ppm)		0.12 ppm (0.10 ppm)
Wastewater	0.070 ppm	0.054 ppm		0.054 ppm
	Measured March 21st 2000			
Sample (1)	6.2 ppm	2.57 ppm		0.31 ppm
		Fresh	One day old	Fresh
Sample (1) – Wastewater 1:1 mix		1.37 ppm (1.31 ppm)	2.07 ppm	0.12 ppm
Sample (1) – Wastewater 1:2 mix		0.92 ppm (0.89 ppm)	1.36 ppm	0.09 ppm

Table 3-12 : Copper speciation in the presence of wastewater (the numbers in parenthesis represent the values in the case of only a dilution effect)

(1) From Table 3-10
(2) Linearly extrapolated from Figure 3-17 at Day 20 after collection (March 14th).

The data show that, immediately after mixing, there is no effect of the mixing with wastewater except a dilution effect. Nonetheless, Sample (1) mixed with wastewater and stored for one day at room temperature showed a 50% increase of dissolved copper content (increased copper content in a 0.45 µm filtrate). This effect would need to be studied further since effluents can be expected to remain half to one-and-a-half days in the wastewater collection system before being treated.

3.5. Discussion

The purpose of the chemical model is to predict the speciation of copper from the composition of the various chemicals that constitute the slurry. Ideally, the chemical model should even be able to predict the effluent pH but such a task is clearly impossible without a precise knowledge of the various slurry components. Besides, the tools in a factory do not operate synchronously so that large variations in effluent composition are to be expected. A chemical model should therefore be considered appropriate if (1) it includes all the species that are actually found in real effluents and (2) it represents accurately the speciation trends of copper.

In order to validate these two points, experimental and predicted speciation of samples (1), (2) and (3) are compared. Additionally, in order to extend the range of this validation, samples (2) and (3) are titrated (see Section 3.3) with sodium hydroxide 0.03 M and the ratio of dissolved copper (0.45 μm filtrate) to total copper is measured over the pH range of interest.

Sample (2) modeled as a Slurry Type A

Though the chemical model could predict that copper is totally dissolved at low pH (below 5), there is some discrepancy between experimental and predicted data in the 5 ~ 7 pH range, which is the one of highest interest. As shown in Figure 3-18, particulate copper appeared at lower pH (pH = 5) than predicted by the chemical model. It is not certain whether this behavior is due to experimental error or the effect of unknown components of the slurry. A similar titration is performed with a slurry made at MIT and composed of 450 ppm of alumina particles (Saint-Gobain Industrial Ceramics - grade # 9245), 10.5 ppm of copper (added as copper sulfate) and a strong acid (supplied in the alumina slurry). Experimental and predicted data are shown in Figure 3-19. Again, some discrepancy is found in the near-neutral pH range, though in this case, predicted dissolved copper was lower than measured dissolved copper.

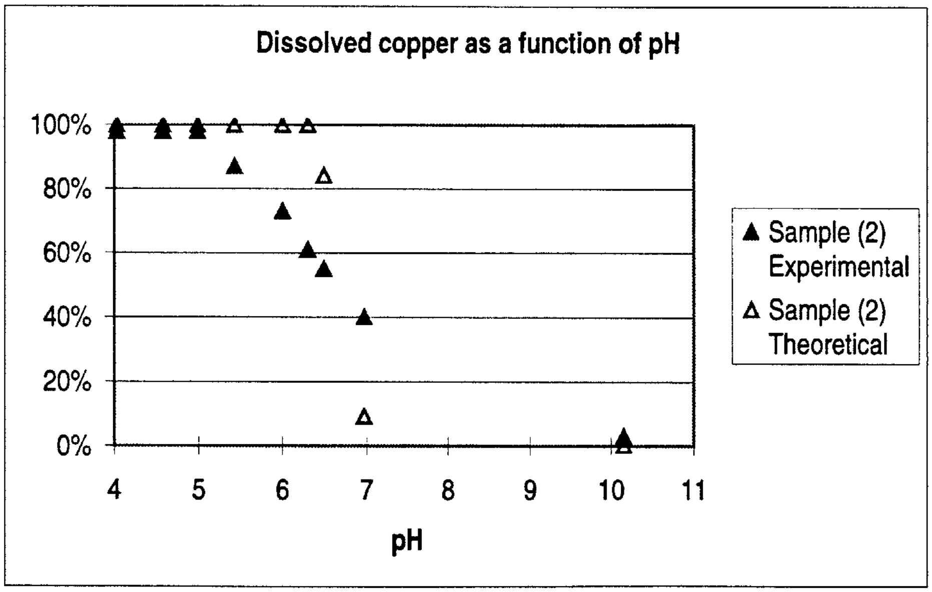


Figure 3-18 : Titration of Sample (2)

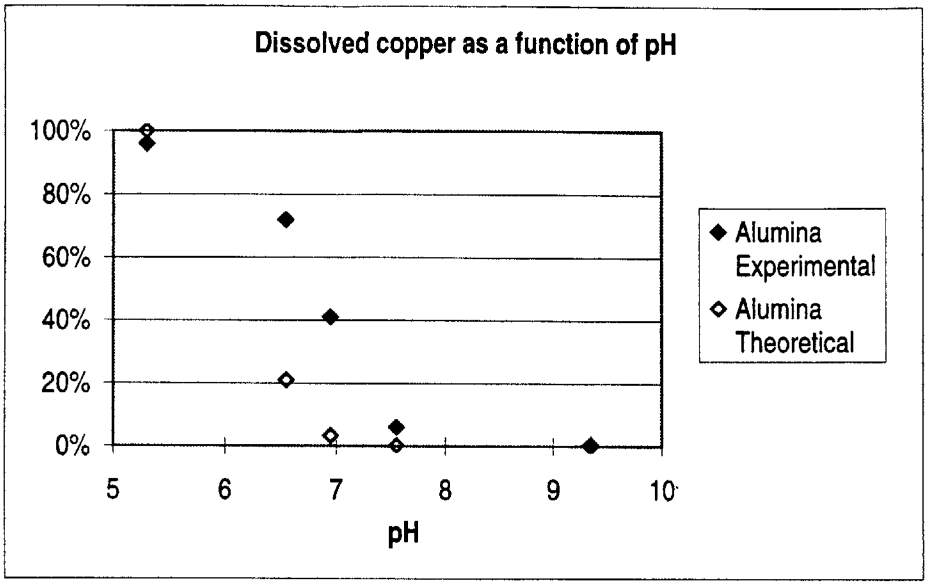


Figure 3-19 : Titration of a copper bearing alumina slurry made at MIT

Samples (1) and (3) modeled as Slurry Type B

Samples (1) and (3) contain a strong complexing agent which is deficient (most probably degraded by the time samples could be tested, as explained in Section 3.3). The chemical model was run to predict copper speciation using the measured total copper concentration of 6.2 ppm, a concentration of complexing agent taken as the measured concentration of strongly complexed copper of 0.9 ppm (15%). The silica particle content is adjusted by trial and error so as to reflect the measured particulate copper of 3.8 ppm (55%) (see Figure 3-20) . However, at pH = 7.1 (pH of the Sample (1)), the model shows that, no matter what the silica particle content may be, the particulate copper (adsorbed on silica or $Cu(OH)_{2,s}$ precipitate) should represent the complement to 100% of the strongly complexed copper, i.e. that no weakly complexed copper can be present at pH = 7.1. This is in contradiction with the experimental measurements (Table 3-10) which show a significant presence of weakly bound dissolved copper (about 25% of total copper).

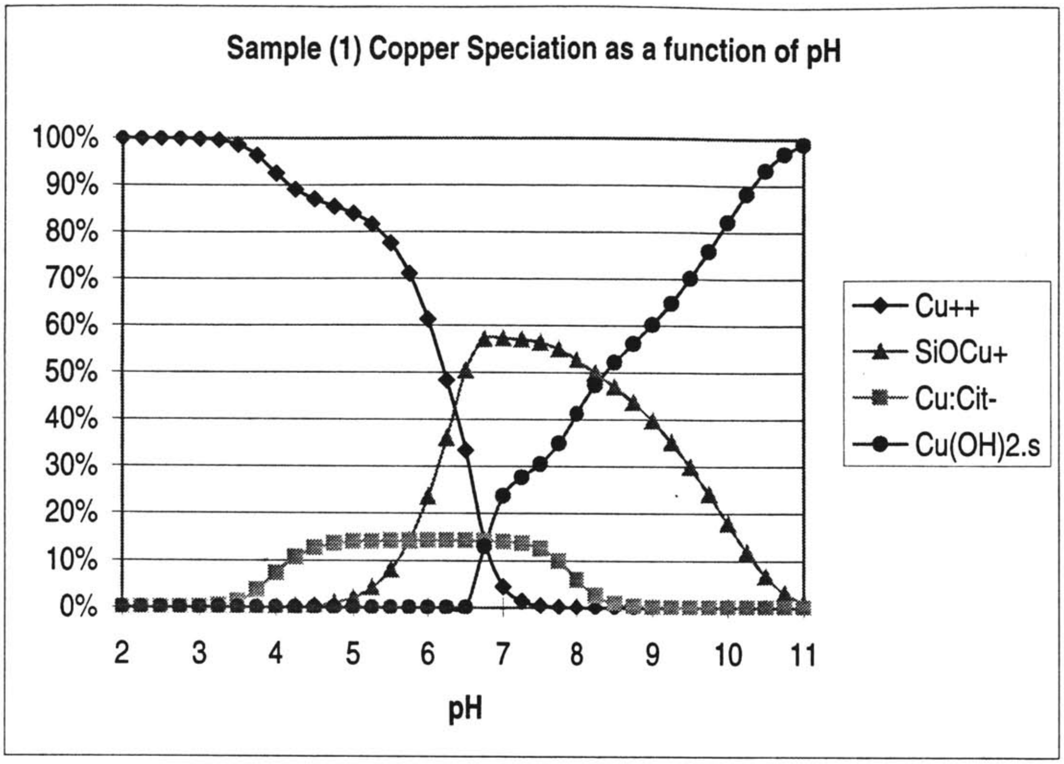


Figure 3-20 : Copper speciation as a function of pH for the following composition :

Copper : 6.2 ppm (9.8.10-5 M)
Citrate : 1.4.10-5 M (15%)
SiOH sites :4.8.10-4 M (silica : 1.27 g/l. corresponding to 8% wt at point-of-use)

One component that is found in effluents, which was not included in the chemical model is ammonia, which can be present in oxide and STI slurries as well as post-CMP clean solutions for oxide, STI and Tungsten CMP [PHILIPOSSIAN 1999]. Even though it is a weak ligand, it could significantly alter copper speciation at medium and high pH because of its abundance. For example, a slurry at pH = 11.5 whose pH is fixed by ammonia content solely would contain 0.63 M of ammonia. Using the facility model (Table 3-7 and Table 3-8) with this ammonia content in oxide and STI slurries gives an ammonia content of $9.5.10^{-2}$ M in segregated CMP effluents (Case 3).

Running the chemical model for Sample (1) with an ammonia content of $9.5.10^{-2}$ M and a silica content of 3.958 g/l as predicted by the factory model shows a significant amount of weakly bound dissolved copper at mid pH range, as seen in Figure 3-21. Presence of large concentrations of ammonia is shown to inhibit precipitation of $Cu(OH)_{2.s}$ at medium to high pH. This phenomenon is consistant with the experimental data on the speciation of copper for Sample (1), where a significant amount of weakly bound copper is found at pH = 7.1.

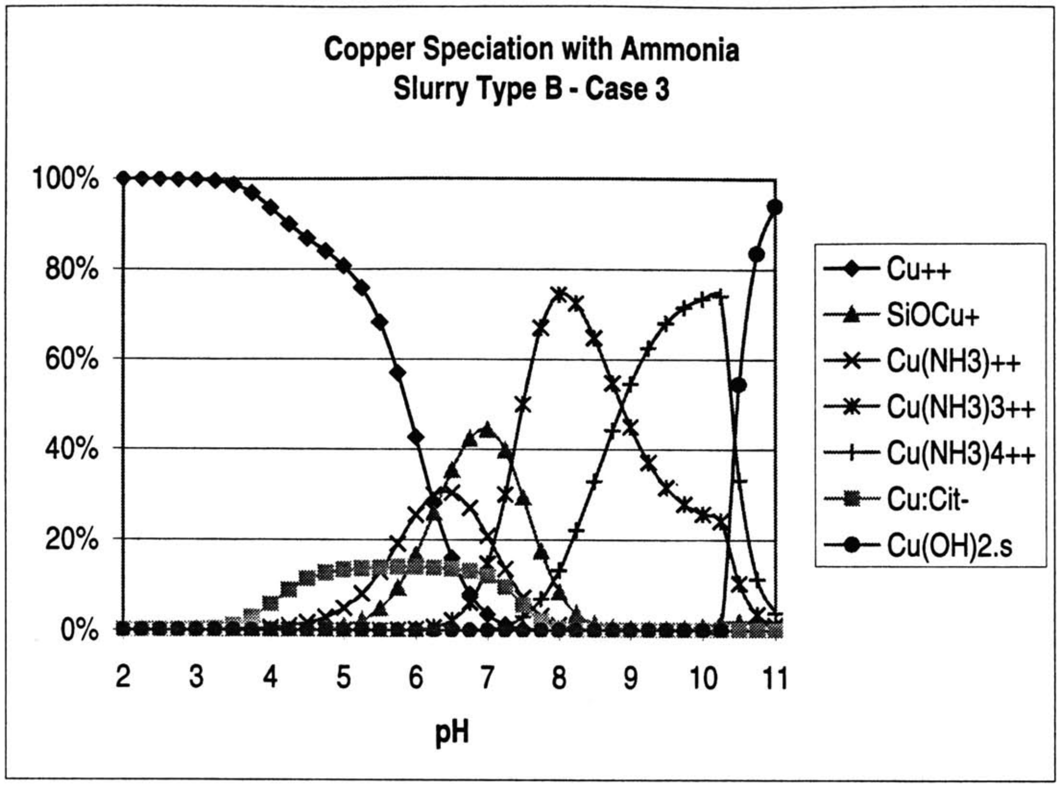


Figure 3-21 : Simulation results for copper speciation with Ammonia (Slurry Type B, Case 3, deficient citrate)

Copper : 6.2 ppm ($9.8.10^{-5}$ M)
Citrate : $1.4.10^{-5}$ M (15%)
Ammonia : $9.5.10^{-2}$ M (0.63 M content in oxide and STI slurries at pH = 11.5)
SiOH sites :$1.5.10^{-3}$ M (silica : 3.958 g/l. corresponding to 25% wt at point-of-use)

Pursuing this point further, a simulation is run for segregated effluents (Case 3) for Slurry Type B in presence of ammonia and with a citrate deficiency. The results are compared in Figure 3-22 with the experimental data collected for the titration of Sample (3), containing 7.8 ppm ($1.2.10^{-4}$ M) of copper and 1.1 ppm ($1.7.10^{-5}$ M) of strongly complexed copper. Predicted and experimental results are in accordance at medium pH but the chemical model shows a higher dissolved copper concentration above pH = 7.5 than the experiments revealed.

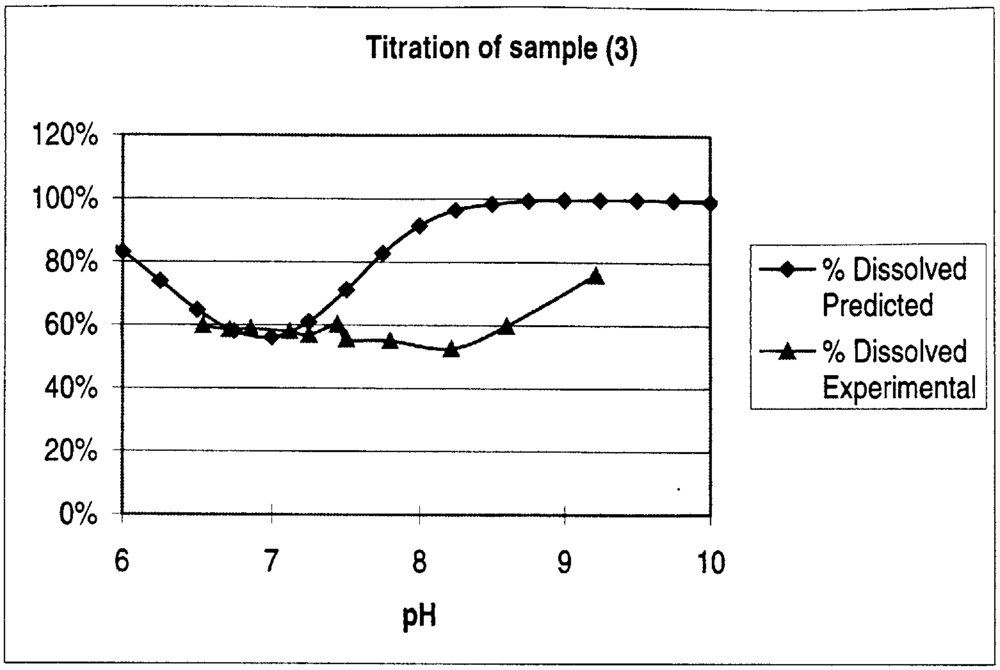


Figure 3-22 : Titration of Sample (3) and simulation results including the presence of ammonia

Copper : 7.8 ppm (1.2.10^{-4} M)
Citrate : 1.7.10^{-5} M (14%)
Ammonia : 9.5.10^{-2} M (0.63 M content in oxide and STI slurries at pH = 11.5)
SiOH sites :1.5.10^{-3} M (silica : 3.958 g/l. corresponding to 25% wt at point-of-use)

Finally, the speciation of copper in segregated CMP effluents (Case 3) with Slurry Type B, where citrate is present at a molar concentration equivalent to that of copper, is presented in Figure 3-23. This simulation is meant to represent the copper speciation in factory effluents, before they have time to degrade. Citrate inhibits adsorption onto silica particles at pH lower than 7 and ammonia prevents precipitation of $Cu(OH)_{2,s}$ at pH higher than 7. Overall the dissolved copper is kept above 75% at all pH values.

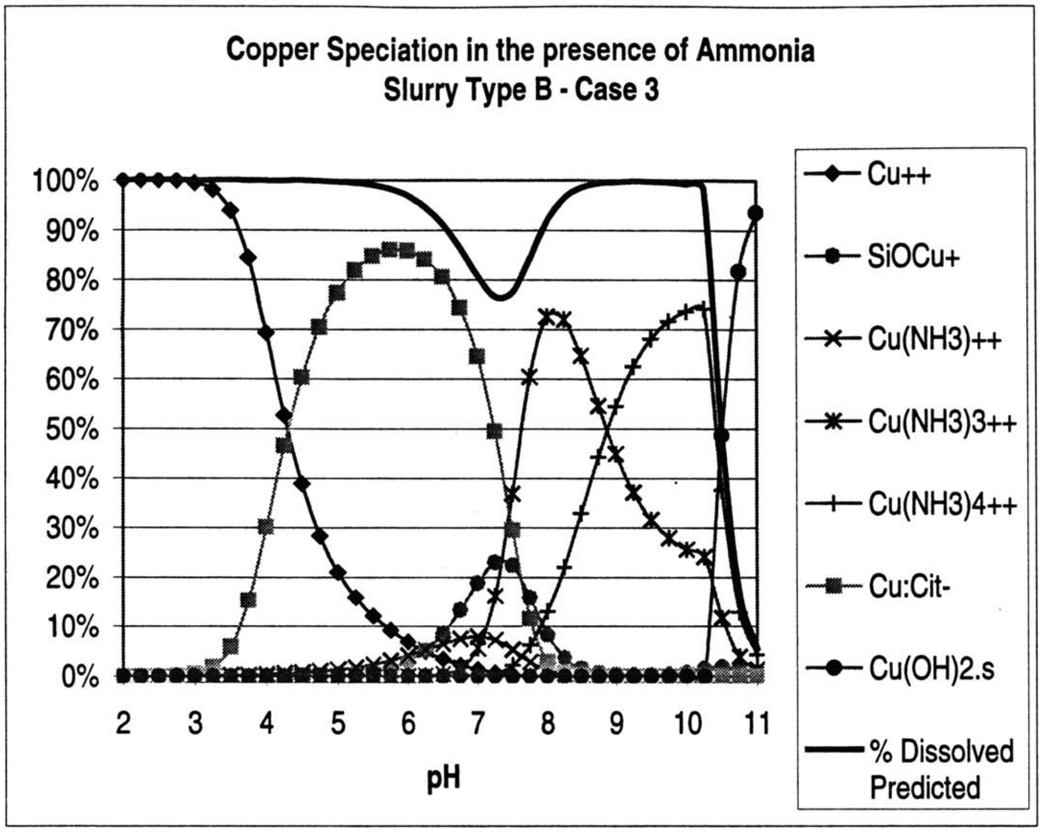


Figure 3-23 : Copper speciation in the presence of ammonia (Slurry Type B – Case 3)

Copper : 5.5 ppm ($8.7.10^{-5}$ M)
Citrate : $8.7.10^{-5}$ M (equimolar with Copper)
Ammonia : $9.5.10^{-2}$ M (0.63 M content in oxide and STI slurries at pH = 11.5)
SiOH sites : $1.5.10^{-3}$ M (silica : 3.958 g/l. corresponding to 25% wt at point-of-use)

4. The Environmental Impact of Copper CMP

4.1. Copper in the Environment

Copper is a prevalent metal in the environment and a necessary nutrient for animal and plant life. An excellent description of the ecological cycling and toxicity of copper can be found in [NRIAGU 1979]. A more recent report by the US Geological Survey [USGS 1997] includes a large amount of data on copper found in the environment, on toxicity of copper on a wide range of organisms and on the biological accumulation in plants.

Table 4-1 lists typical copper concentrations in a variety of natural waters and in drinking water.

Type of water	Copper Concentration (μg/l)	Type of water	Copper Concentration (μg/l)
Groundwater	5	Lakes and Rivers (non-contaminated)	1 - 8
Seawater (oceanic)	0.1 ~ 3	Lakes and Rivers (contaminated)	50 - 100
Seawater (coastal) (1)	5 ~ 50	Wastewater	60 ~ 100 (2)
Drinking water in MA	200 ~ 3200	Drinking water MCL (3)	1300
Rainwater	12		

Table 4-1 : Copper content in a variety of natural waters [From NRIAGU 1979]

(1) Level higher than oceanic levels indicate copper input from rivers as well as anthropogenic sources

(2) Copper is a widely used piping material that slowly leaches into drinking water and can therefore be found in wastewater. Higher levels come from street run-off during rainy periods

(3) MCL = Maximum Concentration Level set by EPA for drinking water. If over 10% of the samples collected are above the MCL, a special treatment technology has to be implemented.

4.2. Bioavailability and Toxicity of Copper

Copper is an essential nutrient (unlike cadmium or lead for example) to organisms and plants and is not a carcinogenic substance. Copper deficiency adverse effects can be observed in organisms that do not have enough copper available to them. On the other hand, toxic effects appear when metal levels in the environment are too high. Therefore, there is a range of copper concentrations which are suitable for organisms to live and develop.

Though copper deficiency is rarely observed in natural environments, excess copper concentrations has been shown to be toxic or lethal to many organisms and a very complete study is presented in [USGS 1997]. What the above report shows is that a concentration of 5 µg/l is safe for almost all species and that some effects such as reduced growth or photosynthesis in algae or teratogenic effects in sensitive species of fish or amphibians may appear at concentrations as low as 5~10µg/l. Large animals such as birds or mammals (including humans) which are exposed to copper from water only through food and drink are more protected from copper toxicity. As an example, the 'average' human body contains about 70 mg of copper and takes up about 3.5 mg of copper per day without adverse effects.

Copper toxicity is strongly affected by copper speciation. Most tests conducted by the EPA are made in laboratories with water relatively poor in strong complexing agents such as humic substances, which are part of the dissolved organic matter present in all natural waters, or anthropogenic complexing agents that can sometimes be found at high levels. As a result, there is a larger concentration of free cupric ion Cu^{2+} in test waters than in natural waters. It has also been shown that toxicity of copper, at last on single-cell organisms, is strongly dependent on free ion concentration rather than on total copper. This is explained by the analysis of the metal uptake process of single-cell organisms [STUMM 1996, pp. 633-637]. Metals are taken from water by functional groups on the membrane of single-cell organisms and taken into the cell by carrier proteins where they are used and then stabilized for excretion. Toxicity and bio-availability of copper is therefore highly dependent on whether the cell surface functional groups are able to grab copper ions.

In natural waters, where copper is usually complexed by natural humic substances or bound to particles, free cupric ions are in concentrations several orders of magnitude smaller than complexed copper and therefore laboratory tests are often conservative, as they should be, and define safe standards. Such standards are used to determine the discharge limits of NPDES permits. What the toxicity studies show is that a discharger with no dilution credit (for example the POTWs in South San Francisco Bay - Sunnyvale, Palo Alto, San Jose / Santa Clara POTWs) should have discharge limits for copper at around 5~10 µg/l, which they do (8.6 µg/l - see Table 2.9). Dischargers into large rivers have a higher limit according to their dilution credit.

4.3. The Impact of Copper CMP Effluents on the Environment

Copper concentration in the effluent of the model facility is 0.26 ppm. In a real factory, water reuse and evaporation (20~40%) are expected to raise concentrations to perhaps 0.5 ppm while the total amount of effluent is reduced in the same proportion. On the other hand, a facility usually gathers several production lines and, since copper metallization is just being introduced, only one would be a copper line. This is for example the case of the IBM Burlington facility, where the introduction of copper metalization is expected to produce about 2 kg of copper per day (before on-site treatment, including baseline copper, i.e. what comes into the facility through the water supply or is generated by other processes) for a flow of effluent of 5 MGD (19 million liters per day), which amounts to 0.11 ppm. Additionally, the treatment system at the IBM Burlington facility removes about 55% of the copper so that effluent concentration is expected to be around 48 µg/l or ppb (900 g/day). For reference, the NPDES limit for the Burlington facility is not concentration-based but mass-based and is 6.86 lbs (3.1 kg) per day (monthly average) and 9.75 lbs (4.4 kg) per day (daily maximum).

The flow of the Winooski river into which effluents are discharged, at Essex Junction where the facility is located, is shown in Table 4-2 [USGS WEB-1].

Latest flow 04/09 13:45	Minimum	Mean	Maximum	80 percent exceedance	50 percent exceedance	20 percent exceedance
6860 ft^3/s	1010 ft^3/s	4710 ft^3/s	15000 ft^3/s	2590 ft^3/s	4260 ft^3/s	6190 ft^3/s
194.3 m^3/s	28.6 m^3/s	133.4 m^3/s	424.8 m^3/s	73.3 m^3/s	120.6 m^3/s	175.3 m^3/s
4434 MGD	653 MGD	3044 MGD	9695 MGD	1674 MGD	2753 MGD	4001 MGD

Table 4-2 : Daily Mean Flow Statistics for 04/09 based on 70 years of record, in ft^3/s

Even at the lowest flow in 70 years, the concentration of copper after dilution for the Burlington plant effluent would be 0.4 µg/l which is a safe level according to the above study [USGS 1997]. Effects due to copper close to the discharge, where concentrations are higher, are hard to evaluate and should result from a case study. Nonetheless, even if copper is weakly complexed, it could be rapidly bound to humic substances in the river.

The problem of dissolved copper discharge may become an issue in the case of discharge into a stagnant water body, such as San Francisco Bay south of the Dumbarton bridge, or into a small river. In that case, the copper concentration calculated from the facility model (0.26 ppm) is clearly too high and would need to be significantly reduced to reach acceptable levels (in the range of 5~10 µg/l in the case of San Francisco Bay south of Dumbarton bridge).

As far as the sludge is concerned, the concentration that is calculated from the facility model can reach 1300 mg of copper per kg of sludge (dry weight basis). In the case of the IBM factory, copper in sludge is calculated to be around 180 mg of copper per kg of sludge because the other lines on the same site generate non-copper bearing solids.

One could therefore argue that the disposal, after conversion to solid waste, of copper CMP sludge into a landfill should be safe since its copper content is in the range of what is accepted for agricultural use (1500 mg/kg as specified in 40 CFR 503.13, 1000mg/kg in Massachusetts). Nonetheless, 40 CFR 503.13 also specifies that no more than 75 kg of copper per hectare (10000 m^2) can legally be applied to agricultural land, rendering the above argument invalid. Indeed, application of copper bearing fertilizers can significantly increase the soil's copper content above the 20 mg/kg found on average in the United States, as described in [NRIAGU 1979, p. 185].

Nonetheless, copper bearing CMP waste is not to be used as fertilizer but disposed of in a landfill. For reference, in 1997, MSW (Municipal Solid Waste) generated in the US amounted to 217 million tons. 61 million tons were recovered and 156 million tons were discharged in landfills or incinerated [FRANKLIN 1998]. 390 thousand tons of non-ferrous metals (zinc, copper but not including aluminum and lead) were discharged and represent 0.25% wt (2500 mg/kg) of municipal waste. The exact copper content of the discharged non-ferrous metals could not be found but is it is probably of the same order than the maximum copper content found in the facility model (1300 mg/kg). Since modern landfills include leachate collection systems as well as several layers of relatively impermeable soil and membranes to prevent contaminants from leaking into the surrounding environment and groundwater, one could argue that disposal of copper CMP waste is no more harmful to the environment that the disposal of municipal waste.

Nonetheless, some older landfill sites have been found to leach significant amounts of heavy metals, including copper. This is for example the case of the Sanitary Landfill Co. site in Ohio or the Spickler Landfill in Wisconsin. Both sites were used as municipal and industrial waste landfills and are listed as superfund sites by the EPA. Groundwater below the Spickler Landfill site contains 2.25 ppm of copper as well as very high concentrations of other heavy metals. Copper leaching from landfill sites therefore remains a possibility, though it is likely that the waste collected in the Spickler Landfill site, for example, were much more contaminated that CMP waste. Indeed, the listing of the Sanitary Landfill Co. and Spickler Landfill site as superfund sites seems to be justified by the leaching of contaminants other than copper, such as cadmium, lead, vinyl chloride and other very toxic chemicals.

Ultimately, the impact on the environment is determined by the performance of the landfill and a more accurate risk assessment analysis would be needed to understand the potential problem posed by copper CMP wastes.

4.4. The Impact of Copper CMP Effluents on the Operation of the Receiving POTW

The main issues to consider when evaluating the impact of copper CMP effluent discharges are the effects on the biological stage of wastewater treatment and the increase of copper in the POTW's effluents and sludge.

A typical wastewater treatment plant includes several stages as shown in Figure 4-1. Large objects are removed by screens, sand-like particles by the grit chamber and then suspended particles are removed by settling in large basins (primary clarifiers). Then, dissolved organic matter is removed in the secondary treatment (whether it be an aerated lagoon, a trickling filter, an activated sludge system or other). In that system, a wide collection of microorganisms degrade the organic matter under aerobic conditions. The suspension is then settled in secondary clarifiers and the supernatant is disinfected before discharge, by chlorination for example. Nitrification / denitrification treatment may also be in place if necessary (many types of systems exist).

As a biological reactor, the secondary stage of the wastewater treatment is sensitive to chemicals contained in the primary influent. The effect of copper on the effectiveness of the biological stage has been studied especially in locations where large electroplating facilities are operated, for example in [CHUA 1997]. It has been reported that inhibition of microorganisms in the activated sludge occurs at concentrations in excess of 1 mg/l. With local limits in the range 0.5 ~ 1.5 mg/l for copper concentrations in industrial discharge and considering the mixing of semiconductor manufacturing effluents with domestic wastewater whose concentration is usually in the range of 60 ~ 100 µg/l, it is rather unlikely that any fouling of the plant would occur because of excess copper discharged from semiconductor manufacturing. Indeed, none of the wastewater treatment plant people interviewed mentioned copper overload as a problem to the biological stage of the plant.

To illustrate this point (see Table 4-3), the Walnut Creek wastewater treatment plant in Austin, Texas, receives an average of 45 ~ 50 MGD of wastewater per day, containing an average of 15 lbs (6.8 Kg) and a maximum of 32 lbs (14.5 kg) of copper per day (1994 ~ 1999 data). That amounts to 40 ~ 85 µg/l. Recent data (1999) show an influent concentration more in the range of 20 lbs (9 Kg) per day, or 50 µg/l.

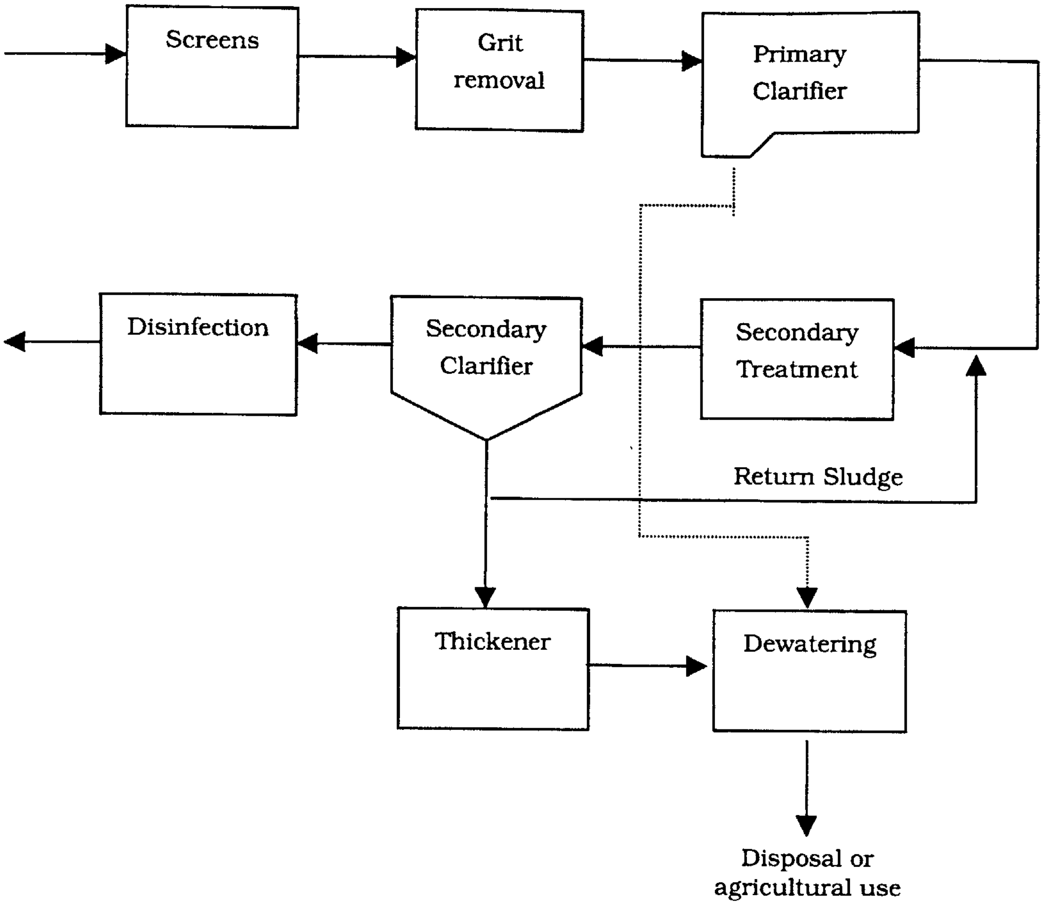


Figure 4-1 : A typical wastewater treatment plant

	Influent Cu (lbs/day	Influent (MGD)	Influent Cu (ug/l)	Effluent Cu (ug/l)	Primary Sludge (mg/kg)	Thickener (mg/kg)	Cu removal
1st 98	12.1	51.08	28.4	7.1	153	258	75%
2nd 98	17.44	41	51.0	8.3	298	358	84%
3rd 98	24.36	44.67	65.3	23.7	180	267	64%
4th 98	15.77	49.25	38.4	6.3	191	338	84%
1st 99	9.62	45.58	25.3	41.2	127	213	-63%
2nd 99	20.84	49.67	50.3	5.5	140	319	89%
3rd 99	32.13	46.25	83.2	33.6	206	404	60%
Average	18.89	46.79	48.84	17.96	185	308	76%

Table 4-3 : Austin Walnut Creek wastewater treatment plant data

Two major contributors to the Walnut Creek plant are the Motorola Ed Bluestein factory and the new Samsung factory. The Motorola Ed Bluestein factory discharges about 2.6 MGD of wastewater per day (5% of the wastewater treatment plant influents). The new Samsung semiconductor factory also discharges into the Walnut Creek wastewater treatment plant. An addition of a copper line in both factories would add 2.5 kg of copper per day (assuming a processing capacity as defined in the facility model, no treatment at the facility) into the wastewater treatment plant influent (an increase of 30%) and raise the concentration to 65 µg/l, well below the level that triggers inhibition of activated sludge microorganisms.

The second issue to consider is the increased copper load in the effluents of the wastewater treatment plant. Removal of copper in wastewater treatment plants has been surveyed and shows that all plants remove 55% or more of the influent copper with 50% of the plants removing 85 % of copper or more [EPA 1982]. Better performing plants such as the San Jose / Santa Clara plant remove up to 96% of influent copper [EKSTER 1996].

Data from the Austin Walnut Creek show copper removal of 76% on average and an average effluent concentration of 18 µg/l. One could therefore expect that a 30% increase in copper concentration in the influent would result in a 30% increase in the effluent. Nonetheless, the issue is not so straightforward. It has been shown that, though particulate copper removal rate can be high, removal of dissolved copper is rather limited as illustrated in Table 4.4 [from EKSTER 1996].

	Copper concentration (ppb) (median)		
Sample Location	Total	Dissolved	Particulate
Primary influent	101	4.2	96
Primary effluent	60	5.4	54
Settled wastewater	58	3.6	53
Secondary effluent	4	1.1	2.9
Final effluent	3.7	3.4	0.2

Table 4-4 : San Jose / Santa Clara wastewater treatment plant data

Note : The only process that significantly removed dissolved copper was the activated sludge stage (3.6 µg/l to 1.1 µg/l). Dissolved copper levels increased again in the final effluent because part of the primary effluent does not go through the activated sludge stage and is fed directly to the subsequent nitrification stage. In the paper by Ekster and Jenkins, dissolved copper is what is in the filtrate of a 0.45 µm filter and particulate copper is what is captured by the filter.

As shown on the above data, particulate copper removal is almost complete while dissolved copper is quite limited (20%). Though these data cannot be generalized, it should be noted that copper CMP effluents containing strongly complexed copper may not be removed significantly by the wastewater treatment plant, particularly when the complexing agent is not easily degradable. This is for example the case for EDTA. On the other hand, citrate being easily biodegradable may show a different behavior in a wastewater treatment plant. In the case of the Austin Walnut Creek wastewater plant, an addition of 2.5 kg/day of strongly complexed copper (non-biodegradable) in the influent of the plant would add 2.5 kg/day or 15 µg/l directly to the wastewater treatment plant effluent, bumping the plant clearly above its NPDES limit of 10 µg/l. In the case of the Sunnyvale wastewater treatment plant, strongly complexed copper at a rate of 1.25 kg/day would go through the system and end-up in the effluents of the POTW. This amount alone (1006 lbs/year) would exceed the Sunnyvale POTW discharge limit of 715 lbs/yr.

Particulate copper would be almost completely removed by the wastewater treatment and end-up in the POTW sludge. At the Austin Walnut Creek POTW (flow 190 000 m^3/day), the amount of sludge generated is probably around 45 tons/day (dry weight basis). An addition of two copper lines generating a total of 2.5 kg per day would, if that copper is in particulate form, increase the copper concentration in sludge by 40 mg/kg (dry weight basis). The fertilizer made from the Austin POTW sludge (product name Dillo Dirt) is far below the Federal and State limit of 1.5 g/kg of copper so that additions from the semiconductor industry would not affect significantly the product quality or its compliance with regulation. On the other hand, the sludge converted to fertilizer by the MWRA in Boston contains 0.9 g/kg of copper, close enough to the State limit for land application of 1000 mg/kg that new sources of copper may cause concern.

4.5. Other Chemicals

The environmental impact of the components, other than copper, which are contained in CMP waste streams was not analyzed in this study. These chemicals include oxidizers, acids, bases, surfactants, corrosion inhibitors etc... An extensive list of such chemicals can be found in [RAGHAVAN 1999] and [GOLDEN 2000].

As far as is publicly known, the chemicals included in copper CMP slurries are not listed in the Priority Pollutant list (Table 2-8) or in the list of Total Toxic Organics that apply to the semiconductor industry (Table 2-7). The facility model that was developed in section 2.2.1 can be used further to assess the impact of other chemicals contained in copper CMP slurries.

4.6. Copper Removal Technologies

Copper removal technologies has been used for decades by the PCB, electronics or metal finishing industries. A general description of these technologies can be found in [NRIAGU 1979, Chap. 6, pp. 123-169]. These include precipitation (lime precipitation for example), reverse osmosis, ion exchange, electrodialysis and other electrolytic processes.

Newer technologies have also been investigated specifically for the treatment of CMP effluents, which present the difficulty of containing a strong oxidizer, suspended particles of very small size and copper that may be strongly complexed. Such technologies are proposed by companies such as Kinetico [KIRMAN 1998], Hydromatics, US Filters [MENDECINO 1998] or Microbar [GOLDEN 2000].

Additionally, electrocoagulation and electrophoretic cross-flow filtration are being studied at the University of Arizona [RAGHAVAN 1999] [LUDKE 2000] and precipitation of copper on ions particles followed by electromagnetic removal was studied at MIT [MIT Patent Application].

The choice of a treatment system is dependent on many different factors : the speciation of copper in the effluents, the desired performance of the copper removal system and economic considerations.

The speciation of copper in the copper CMP effluents has a strong influence on the choice of a treatment system. For example, Figures 3-9, 3-10 and 3-11 show that copper cannot be removed in a lime-precipitation system because $Cu(OH)_{2,s}$ formation is inhibited either by the complexation of copper or by its adsorption onto silica particles. Microfiltration membranes may be incompatible with the slurry oxidant [KIRMAN 1998]. Ion exchange resins or chelating polymers (which are similar in principle to Chelex resin) may prove inefficient to remove strongly complexed copper, such as citrate or EDTA (see Section 3.4.1). As a result, the choice of a treatment system may be very difficult and limit the semiconductor manufacturer's options to change slurry chemicals since a universal copper removal system remains to be found.

Required performance for the copper removal system is very site-specific. For example, direct dischargers having copper limits in effluents as low as several 10 µg/l will need high removal performance while indirect dischargers may have more leeway.

From an environmental protection standpoint, the complete removal of copper from both effluents and sludge and subsequent recovery of the metal is the best option. It is the objective of systems such as the ones proposed by US Filters [MENDECINO 1998] or Kinetico [KIRMAN 1998] for example. Slurry particles are removed by microfiltration and the solids-free filtrate is passed through an ion exchange column to produce a copper-free effluent. Copper is periodically extracted from the ion exchange resin and recovered by electrowinning. If no copper is to be present in the sludge generated by microfiltration, then this operation should be conducted below pH = 5 (see Figures 3-9 and 3-10). Additionally, the ion exchange resin should effectively remove dissolved copper at low pH, which may be difficult. Flexibility, reliability and cost of such system have yet to be validated for large scale copper metalization operations. Additionally, the resin recycling process that uses concentrated acid for copper removal may generate another class of unwanted wastes.

Another option, if one is convinced of the efficacy of the receiving landfill, is to design a system that will precipitate copper into the waste sludge. This is the objective, for example, of the Enchem™ system proposed by Microbar [GOLDEN 2000]. In that case, the addition of a chelating polymer binds to the dissolved copper and flocculates, producing a copper bearing sludge and a copper-free effluent. That would require that the chelating polymer should effectively remove copper, which may be difficult if it is strongly complexed.

In both types of systems, the efficiency of the copper removal chemical (ion exchange resin or chelating polymer) may be strongly dependent on the speciation of copper. It is for example doubtful that EDTA-complexed copper can be treated at all, and effluents containing citrate may need to be treated at very low pH. The adsorption of copper on silica particles may also strongly affect copper removal performance for the first type of system.

As a result, the copper removal system should ideally treat segregated copper CMP effluents at below pH =4 for slurries that contain no complexing agent, and below pH = 3 for slurries that contain citrate (see Figures 3-9 and 3-10), before they are mixed with high pH streams.

4.7. Environmental Policy Choices

The choice of a CMP waste treatment system and, to some extent, of slurry chemicals is strongly influenced by regulatory and economic concerns. There are currently two main classes of systems available today (microfiltration/ion exchange or flocculation), as described in Section 4.6 to satisfy two distinct environmental policy choices.

The first type of system, if properly used, should produce copper-free sludge and effluents, thus reducing the environmental impact of copper CMP effluents to a minimum. Such a system, with a capacity of 50 GPM (adequate for the treatment of the segregated effluents of the model facility described in Section 2.2), is nonetheless expected to cost $500 000 per year [MENDECINO 1998].

The second type of system is expected to be cheaper to own and operate because of its simplicity, but presents the risk of contamination of the ultimate disposal site because copper is present in the sludge.

The choice for the semiconductor manufacturer is therefore between a costly system that has the potential of eliminating all environmental concerns and a possibly cheaper one that presents the risk, however remote, of requiring the very costly clean-up of the sludge disposal site in the future. Aside from cost and environmental impact issues, the drive to reuse or recycle water inside the semiconductor facility may become an important criterion for treatment equipment selection.

The choice of slurries may also be influenced by regulatory concerns. The development of environmentally-benign slurries is one of the targets of the ITRS Roadmap for Semiconductors [ITRS 1998, p. 36 Table 35] for the year 2000. As an example, the use of EDTA should be avoided because of its persistence in the environment, while citric acid is easily biodegradable. Surfactants used to keep slurry particles in suspension are also a concern since they present adverse effects such as the reduction of oxygen uptake by the gills of fish.

Conclusions

Through the analysis of the CMP process and the modeling of a typical facility, this study shows that copper removal before discharge is necessary to achieve compliance with current environmental standards for direct discharge or future, more stringent, local limits for indirect discharge. It also shows that copper bearing sludge, considered non-hazardous today (provided it has not been in contact with electroplating rinse waters), should not have adverse effects on the environment if disposed of properly.

The development of a chemical model to determine copper speciation in effluents at various nodes of the facility waste collection system shows that adsorption of copper on silica particles (coming from other CMP processes) or the formation of $Cu(OH)_{2,s}$ precipitate may complicate the treatment process in systems that remove dissolved copper. For such systems, it is necessary to treat effluents as early as possible in the facility waste collection system, before mixing them with higher pH post-CMP clean solutions or effluents from other CMP processes. This renders CMP tools that can segregate process effluents, and particularly those from the copper polishing platen, highly desirable.

The analysis of copper speciation also shows that synergies between the copper CMP, other CMP and post-CMP clean solutions can be advantageously used to limit overall chemical use, thus reducing consumables cost, waste treatment cost and environmental impact.

For example, the pH stabilizing acid in the copper CMP slurry can be chosen as a complexing agent (for example citric acid); the post-CMP clean solution can include citric acid that will remove adhered alumina particles from the wafer but also keep copper in solution for an easier treatment, rendering the complexing agent of the slurry unnecessary; ammonia from oxide, STI or tungsten slurries can prevent $Cu(OH)_{2,s}$ formation at medium and high pH and may eliminate the need for a complexing agent in copper CMP slurries

There are numerous such possibilities that can reduce the cost and environmental impact of copper CMP. It is therefore highly desirable that slurries used in different CMP processes be designed together, as a package, and ideally adjusted to take into account the constraints of a specific plant.

References

[BRAUN 1999]	Alexander E. Braun, Aluminum persists as copper age dawns, Semiconductor International, Aug. 1999, pp. 58-66
[CHANG 1996]	C.Y. Chang and S. M. Sze, ULSI Technology, Mc Graw Hill 1996
[CHUA 1997]	H. Chua et al, Sub-lethal effects of heavy metals on activated sludge microorganisms, Chemosphere Vol 39, No 15, pp. 2681-2692
[DELANEY 1989]	J.R. Delaney, Electronic Materials Handbook, Volume 1 Packaging, ASM International, 1989
[EKSTER 1996]	Alex Ekster and David Jenkins, Nickel and Copper Removal at the San Jose / Santa Clara Water Pollution Control Plant, Water Environment Research, Vol 68, number 7, Nov.-Dec. 1996
[EPA 1982]	Fate of Priority Pollutants in Publicly Owned Treatment Works, EPA #440/1-82/303, Sep. 1982
[EPA 1983]	Guidance Manual for POTW Pretreatment Program Development, October 1983
[EPA 1988]	Copper : Water Quality Standards Criteria Summaries : Compilation of State and Federal Criteria, EPA# 440588027
[EPA 1999-1]	National Recommended Water Quality Criteria – Correction, EPA-822-Z-99-001, Apr. 1999
[EPA 1999-2]	Introduction to the National Pretreatment Program, EPA-833-B-98-002, Feb. 1999
[EPA WEB-1]	http://www.epa.gov/5Super/npl/ohio/OHD093895787.html
[EPA WEB-2]	http://www.epa.gov/5Super/npl/wisconsin/WID980902969.html
[EPA WEB-3]	http://www.epa.gov/epaoswer/general/orientat/
[EPA WEB-4]	http://www.epa.gov/ooaujeag/projectxl/learnabt.htm
[EPA WEB-5]	http://www.epa.gov/ooaujeag/projectxl/ibm2/index.htm
[FRANKLIN 1998]	Franklin Associates, Characterization of Municipal Solid Waste in the United States, 1998 update, prepared for the EPA, EPA #350
[GOLDEN 2000]	Josh H. Golden, CMP Wastewater Treatment, Chemical-Mechanical Planarization for ULSI Multilevel Interconnect Concference, Mar. 2-3^{rd} 2000, pp. 305-308
[GU 1999]	Youfan Gu, Paul Dozoretz, Jay Bhakta and Fuodoor Gologhian, Management of TEOS LPCVD process effluents, Solid State Technology, Jul. 1999, pp.151-156
[HALL 2000]	Maurice Hall, MWRA, Private Communication
[IBM WEB-1]	http://www.chips.ibm.com/sa27/index.html (IBM Research Web Site)
[ITRS 1997]	International Technology Roadmap for Semiconductor – 1997
[ITRS 1998]	International Technology Roadmap for Semiconductor – 1998 update

[JOINER 2000] Jeff Joiner, DMOS 4 200 mm Conversion Water Optimization Strategy, Jeff Joiner, Texas Instruments, ERC Tele-seminar Mar. 23rd 2000

[KIRMAN 1998] Lyle Kirman, Copper Removal from CMP Wastewater, CMP Users Group, Environmental Safety and Health Issues in CMP Workshop, NCCAVS, Sematech, ERC, Apr. 1st 1998

[LEHMAN 1999] Lehman Brothers : A brighter Polish : Trends in the Chemical Mechanical Planarization Industry, Sep. 9th 1999

[LIN 1998] X. W. Lin and D. Pramanik , Future Interconnect Technologies and Copper Metalization, Solid State Technology, Oct. 1998, pp. 63-79

[LINEBACK 1999] J. Robert Lineback , Semiconductor Business News, February 1st 1999, Move to Copper picks up speed, but process still needs work

[LUDKE 2000] Jamie Ludke, CMP Wate Treatment : Electrophoretic Cross-Flow Filtration, ERC Teleseminar, May 4th 2000

[MAZUREK 1999] Jan Mazurek, Making Microchips, Policy, Globalization, and Economic Restructuring in the Semiconductor Industry, MIT Press, 1999

[MENDECINO 1998] Laura Mendecino and Paul Thomas Brown, The Environment, Health and Safety Side of Copper Metallization, Semiconductor International, Jun. 1998, p. 105-110

[MOREL 1993] Francois Morel and Janet Hering, Principles and Applications of Aquatic Chemistry, John Wiley and Sons, 1993

[NARA WEB-1] http://www.access.gpo.gov/nara/cfr/index.html.

[NRIAGU 1979] Jerome O. Nriagu, Copper in the Environment, John Wiley and Sons, 1979

[OMARA 1998] Omara Associates, IC Planarization by Chemical Mechanical Polishing, 1998

[PHILIPOSSIAN 1999] Ara Philipossian, CMP Consumables, Fundamentals of Chemical-Mechanical Polishing, NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing / International Sematech, Nov. 15-16th 1999

[RAGHAVAN 1999] Fundamentals of Chemical-Mechanical Polishing, NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing / International Sematech, Nov. 15-16th 1999

[RYU 1999] Changsup Ryu, Haebum Lee, Kee-Won Kwon, Alvin L.S. Loke and S. Simon Wong, Barriers for Copper Interconnections, Solid State Technology, Apr. 1999, pp. 53-56

[SEDLAK 1997] David Sedlak, Jonathan T. Phinney and William W. Bedsworth, Strongly Complexed Cu and Ni in Wastewater Effluents and Surface Runoff, Environmental Science and Technology, Vol. 31, No. 10, 1997

[SINGER 1997] Peter Singer, Copper goes mainstream : low-k to follow, Semiconductor International, Nov. 1997, pp. 67-70

[SINGER 1998] Peter Singer, Tantalum, Copper and Damascene : the future of interconnects, Semiconductor International, June 1998, pp. 90-98

[STEIGERWALD 1997] John M. Steigerwald, Shyam P. Murarka and Ronald J. Gutmann, Chemical Mechanical Planarization of Microelectronic Materials, John Wiley & Sons, 1997

[STUMM 1996] Werner Stumm and James Morgan, Aquatic chemistry, John Wiley and Sons, 1996

[SUN 2000] Yuxia Sun, The Colloidal Chemical Investigations Pertaining to Cu-CMP, PhD Thesis, University of Arizona at Tucson, May 2000

[SUN 2000-2] Yuxia Sun, University of Arizona at Tucson, Private Communication

[THOMPSON 1993] Carl V. Thompson and James R. Lloyd, Electromigration and IC Interconnects, MRS Bulletin Dec. 1993, p. 22

[USGS 1997] Copper Hazards to Fish, Wildlife and Invertebrates : A Synoptic Review, Biological Science Report # USGS/BRD/BRS-1997-0002, 1997

[USGS 1998] Toxicity of proposed water quality criteria-based mixtures of 11 inorganics to Ceriodaphnia Dubia and Fathead Minnow, USGS/ECRC-1998-001, Mar. 1st 1998

[USGS WEB-1] http://bowdnhbow.er.usgs.gov/rt-cgi/gen_stn_pg?station=04290500

[ZORICH 1998] Bob Zorich & Mary Majors, Solid State Technology, Sep. 1998, Safety and Environmental concerns of CVD copper precursors, p 101