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The Fate of Dosed Copper to Inhibit Nitrification in Chloraminated Water Distribution System

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ABSTRACT

Chloramine as a secondary disinfectant has been widely used by many water utilities around the world especially in a distribution system requiring a longer retention time such as the 600km long Goldfield water distribution system of Western Australia. Chloramine is selected mainly due to its better stability and low by-products over other disinfectants. However, it is reported that under nitrifying conditions, chloramine residual could drop dramatically. Consequently the required disinfectant concentration can not be maintained. Nitrification, microbial process, is known to be causing rapid depletion of the chloramine residual and enhancing the growth of heterotrophic bacteria. In preliminary studies conducted in Water Corporation, copper at concentrations of 0.25mg/L has been found to be effective against nitrifiers. A concentration of 0.25mg/L as copper is achieved by directly dosing into the main pipeline at the outlet of the Cunderdin reservoir. Nonetheless, the preferred copper concentration can not be maintained as gradual decrease of dissolved copper in bulk water has been encountered along the pipeline. This research aimed to investigate fate of copper in bulk water and distribution system. Three fundamental mechanisms leading to copper loss had been investigated: gravitational sedimentation, adsorption onto wall or biofilm and mineral ions induced aggregation. During investigation of these mechanisms, potential controlling factors (pH, alkalinity, DOC, mineral ions…etc) were brought into a series of experiments as variables. Hardly can free cupric ions or copper hydroxide particles exist in bulk water samples. It was found that major Cu-containing forms are inorganic and organic copper compounds. Solubility of inorganic copper compounds is in equilibrium with calcium carbonate buffered system while organic copper compounds are controlled by organic matters and dissolved organic carbon in drinking water. Minerals such as ferric/ferrous ions and calcium ions contained in the distribution system can aggregate various copper species in bulk water to form particles. Consequently, it can lead to sedimentation or deposition onto walls or sediments. Wall adsorption had been simulated using glass fibre (GF) filters in the laboratory. GF filters were found able to absorb various forms of dissolved copper and copper compounds, though further work needs to be done to investigate the real pipe surface adsorption and complete the adsorption model. Historical data from the field had been analysed.

Combined with laboratory results, it shows that both adsorption and mineral ions induced aggregation are contributing to the loss of copper in the distribution system. However, to further quantify these two mechanisms respectively and build up a comprehensive model, more field data are needed and more laboratory work needs to be done. Copper with different forms will be brought into inhibition experiments in the next stage of research in order to find effective form(s) against nitrifying bacteria. Based on the current achievement on the fate of copper, an inhibition strategy is suggested at the end of this thesis.

Keywords: chloramine, water distribution system, nitrifying bacteria, inhibition, fate of copper, aggregation, adsorption

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Weixi Zhan

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Drinking Water Disinfection

1.1.1 The Advantages of Applying Chloramine to the Final Disinfection Stage

Chlorine and chloramine have been popularly used in the treatment of drinking water. In drinking water treatment plants, both of these chemicals are applied as a disinfectant to control of taste and odour, the oxidation of organic and inorganic substances and the suppression of biological growth in plants. In the course of water distribution network, they provide disinfectant residuals to maintain water quality against microbiological contamination.

As a stronger disinfectant, chlorine is used in water treatment processes more effectively than chloramine. Nevertheless, chloramine is preferred as a final disinfectant in long water distribution system for controlling microbial growth and disinfectant by-products (DBPs). Compared with chlorine, chloramine's priorities are considered chemical stability (lower decay rates), sustained disinfection capability, low DBPs such as THM, control of biofilm regrowth and minimal taste and odour (Kirmeyer P.E. et al., 2004). In a long distribution system, the above factors are regarded as the main mechanisms contributing to the decay of disinfectant's residuals.

1.1.2 Monochloramine Decay in the Distribution System

Chloramine is formed by combining free chlorine and ammonia. Chloramine species generally include monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3). From a disinfection point of view, monochloramine is the preferred form, however, it is inherently unstable in natural pH environments. Auto-decomposition caused by chemical reactions involved in hydrolysis, disproportionation andredox reactions are inevitable. They are controlled by temperatures, Cl_2/N ratio, pH and some redox chemicals existing in natural water (Peter J. Vikesland et al., 2001). On the other hand, nitrifying bacteria surviving in pipelines were proved to be one of the major contributions to triggering and accelerating monochloramine's decay. Nitrifiers present in water consume free and combined ammonia from chloramine and convert it to nitrite (NO_2^-) and nitrate (NO_3^-) through microbiological reactions (Kirmeyer P.E. et al., 2004). Nitrification is known to accelerate chloramine decay dramatically. Once the disinfectant residuals decrease to a low level in the drinking water distribution system, the quality of service water deteriorates and the health of users is undoubtedly threatened.

Chloramine is widely used as a final disinfectant in many water utilities in USA, Australia and European countries. However, considerable chloramine decay caused by nitrification in drinking water distribution system was extensively reported and desired disinfectant residual was found difficult to maintain. Goldfield Water Distribution System (GWDS) in Western Australia (WA) was chosen in this research, where chloramine has been used as a final disinfectant. The main pipe is about 600 km long above ground with very big water temperature variation (between 5-50^{o}C). Severe microbiologically-assisted chloramine decay has been encountered in such a long service pipeline (600 km). Disinfectant residuals are found difficult to maintain above preferred levels especially when residuals have to penetrate the whole pipeline.

1.2 Inhibition against Microbiological Decay: Laboratory Experiments and Health Concerns

1.2.1 The Effective Inhibition Achieved In the Laboratory

Heavy metals such as silver and copper have been proved to be effective to kill or inhibit micro-organisms including nitrifying bacteria. Arumugam Sathasivan (Arumugam Sathasivan et al., 2005) introduced the microbial decay factor (F_m) to quantify the microbiologically assisted chloramine decay in bulk water. The difference between two decay coefficients (decay coefficient in the unprocessed sample and that in the inhibitor added sample) indicated the relative contribution of microbiologically assisted chloramine decay to total chloramine decay in bulk water. The ratio of microbial decay rate (k_m) to chemical decay rate (k_c) is equal to microbial decay factor (F_m). Water samples drawn from C-K extension reticulation were used in inhibition experiments recently (Appendix A). The relatively high F_m indicated the severe microbiological decay and effectiveness of inhibition.

k_c: chemical decay rate coefficient
k_m: microbial decay rate coefficient
F_m: microbial decay factor $F_m = k_m/k_c$
0.1mg/L silver nitrate was dosed as the inhibitor

1.2.2 The Inhibition by Cupric Sulphate and Health Concerns

Copper is used in some water utilities as an inhibitor and demonstrates fair ability to control micro-organisms and bacteria (fungi, algae). It has been successfully used as a biocide in water dams or reservoirs (Eric Van Hullebusch et al., 2003). In laboratory trials, copper was found to be toxic (affecting the metabolism and/or assimilation) to nitrifying bacteria including other micro-organisms. The allowable concentration of copper in water is 2mg/L. This standard is much more than 0.25mg/L, which is applied to control nitrification in this research, so, this copper concentration is assumed to be acceptable in the drinking water. Department of Public Health (WA) has approved the use of copper up to a level of 0.25mg-Cu/L and this research was based on this approved concentration.

1.3 Challenges Encountered in the Field Application of Copper Inhibition

Water Corporation conducted field and laboratory experiments to test the feasibility and efficacy of copper. Copper was dosed in two locations, one in the Merredin reservoir (2005) and the other in the reticulating pipes at the C-K extension. Trials at Merredin suggested that it is possible to keep copper concentration in bulk water to the required level after about two weeks of saturation. Copper sulphate ($CuSO_4$) dosing in the C-K extension was started in April 2006 and has been continuing ever since. Copper sulphate solution is directly dosed into the main at the outlet of the Cunderdin reservoir. Initially a flow paced to achieve 0.25mg-Cu/l dosage in bulk water. Later the concentration was adjusted to a higher level. It was expected that there would be some delay in achieving the required copper concentration in further points of the distribution system from the experience at Merredin reservoir, which took about two weeks to stabilize the copper concentration to the required level. In the C-K main, it was found that soluble copper concentration gradually decreased along distribution system to an unexpected low level. Consequently, the desired copper concentration can not be maintained to inhibit the growth of nitrifying bacteria at further points of distribution pipe lines. This will lead to the acceleration of decay of the disinfectant residuals and accumulation of copper in the main in the form of sediments or in the form of absorbed metals on the surface. How to maintain the desired copper concentration during the water travelling along the distribution system has become a critical issue in order to protect chloramine from microbial caused decay. To solve this question, an understanding of fate of copper in distribution system is indispensable. Factors controlling copper solubility in bulk water and distribution system have to be investigated first.

1.4 The Objectives of the Research and Scope of the Study

As already mentioned, it is critical to maintain relatively high soluble copper concentration in order to protect monochloramine and ammonia from severe nitrifying decay in the distribution system. This research focuses on “the fate of copper” in the bulk water and distribution system as well as potential factors controlling it.

Theoretically, the “fate of dosed copper” in the distribution system could be three: sedimentation, deposition or biofilm absorption and dissolved forms. Apparently a decrease in copper concentration can be caused by sedimentation and surface deposition. As it was impractical to draw biofilm samples from the distribution system, bulk water samples were chosen as major targets in which possible controlling factors in the drinking water system were simulated and investigated. Mechanisms leading to copper sedimentation, deposition or solution have been explored and a preferred copper inhibition strategy is suggested for water utilities.

The following aspects were investigated in this research:

- Fundamental forms of Cu-containing substances in bulk water and distribution systems
- Factors controlling the fate of copper in bulk water and distribution systems
- Mechanisms involved in “fate of copper” in bulk water and distribution systems

The analytical work undertaken strictly followed standard methods for water and wastewater (APHA, 2005).

1.5 Research Significance

With the increased drinking water standards required by World Health Organization (WHO) and US environmental protection agency, more and more stringent standards enforced on DBPs levels force more water utilities to switch to chloramination. Surveys report that 60% of US water treatment facilities use chloramine as a final disinfectant (Kirmeyer P.E. et al, 2004). As mentioned previously, chloramine as a secondary disinfectant has many advantages compared over chlorine such as lower level DBPs (disinfectant by-products) and more stable residuals.

However, confronting chloramines’ potential vulnerability to the microbiological process known as nitrification, many utilities in Europe have given up using chloramine as a disinfectant. The innovation to apply copper to control or inhibit the growth of nitrifiers in drinking distribution systems would definitely change the way chloramine will be seen. Unfortunately, copper concentrations in bulk water were found to decrease with distance especially in pipe lines. The reason for the “disappearance” of copper from bulk water solutions and what caused chloramine decay were not clear. This research was dedicated to the fate of copper in the distribution system and investigated various mechanisms controlling copper solubility. In conclusion, suggestions about how to build up effective inhibition and chloramine stability are suggested for water utilities.

1.6 Compositions of the Thesis

This research was triggered by challenges confronted when a nitrifying inhibition strategy was applied in chloraminated water distribution systems.

Chapter 1 begins with the advantages and disadvantages of choosing chloramine as a final disinfectant. The strategy of nitrifying inhibition by copper is introduced and copper loss encountered in distribution system is discussed. The main purpose and significance of this research are highlighted in this chapter.

Chapter 2 recounts valuable information reviewed from previous research related to the theme of the thesis. Critical points from historical research have been reinforced.

Chapter 3 details sample sources and general methodology about copper analysis involved in every experiment.

Chapter 4 and Chapter 5 form the main body of this thesis. Chapter 4 gives details of experiments undertaken in the research. Based on three fundamental mechanisms controlling the fate of copper, a series of experiments was undertaken to assess each. Results and conclusions are given for each experiment. Chapter 5 analyses the historical data collected in the field. Comparisons between laboratory results and field data are made.

Chapter 6 summarizes the achievements of the research and suggestions for further work and inhibition strategies for water utilities are given.

This thesis ends with a list of references.

CHAPTER 2

LITERATURE REVIEW

Chloraminated water is usually maintained at pH8.0 to increase the stability of chloramine. If no other complexes are considered, at pH of 8.0 there can only be around 3 μg/L of Cu^{2+} exist in solution (using solubility product of $Cu(OH)_2$ as $10^{-19.3}$). That means this concentration will be achievable in a pure water rather than in distribution system water. Meanwhile, natural organic matters (NOM) and ammonia can form complexes with copper to make NOM-Cu or ammonia-Cu complexes. Because of these copper related reactions, three basic forms of copper can exist, the sediment form (due to precipitation), wall or biofilm associated form (due to adsorption or deposition) and soluble forms in bulk water. Copper sediments include $Cu(OH)_2$, CuO, and other particles formed by copper binding or aggregating with inorganic or organic substances such as iron, manganese and NOM. Excretions (Extracellular polymers, enzymes etc) of nitrifiers and some microbes (living in the biofilms, sediments and bulk water) can combine with copper to neutralize copper's effectiveness. Soluble copper may appear in various forms: organic or inorganic copper compounds and cupric ions. In order to further understand this aspect a detailed literature review had been conducted, details of which are given below.

In chloraminated supplies, ammonia and chlorine are added to form chloramine. In order to maintain the chemical stability of chloramine and maintain the water slightly encrustive (scale forming), pH is controlled at 8.0. Sawyer and McCarty (Clair N. Sawyer, 1978) quoting Sillen and Martell (1971) gave a series of equilibrium constants for Cu-Ammonia complex formations. The higher the pH, the more will be the amount of ammonia present. At pH 8.5, the fraction of ammonia present will be 5% of total ammonia-N. Current total-N (NH_3+NH_2CL) levels are in the range of 0.8mg/L or 47μM. Five percent of 0.8mg/L is only 0.04mg/L or 2.35μM. At this concentration the predominant species will be Cu^{2+} (about 95% of copper). This calculation was made assuming only Cu^{2+} and ammonia were present in water. With possible combinations of other metals and ligands present in the water, it is expected that the Cu- NH_3 complex will be of much lower in concentration. Therefore, the complexation of copper with ammonia can be neglected.

In addition, Vernon L. Snoeyink (1980) suggested that when water is buffered by carbonate (similar to drinking water distribution system that has carbonate), there could be additional complexes ($CuCO_3^0$, $Cu(OH)_3^-$) formed and these are in equilibrium with $CuO_{(s)}$ (tenorite) and not $Cu(OH)_{2(s)}$. Probably, this ($CuO_{(s)}$) is what coats the surface of (or biofilms in) pipelines and reservoirs. The complexes will increase the copper concentration in solution. The concentration of copper in soluble forms of Cu^{2+}, $CuCO_3^o$, and $Cu(OH)_3^-$ at pH 8 is found to be around 60-70ug/L.

A 0.45µm membrane is usually used to separate particles and dissolved substances. In the field investigations, it was used to separate particulate and dissolved forms. However, the particle size of $Cu(OH)_2$ is reported to depend on pH values of the solution. At pH 8.0, the particle size is only 385nm (R.O.SKOLD, 2001). Probably this explains why copper hydroxide particles were not trapped in the field filtration.

Some further studies (Sigg, et al 2000) suggested that copper has a high affinity to bind particulate material, so copper in surface water is often associated with suspended solids. Furthermore, sediments accumulated by these particulates are considered as potential sinks for heavy metals. Major metal-binding phases in sediments are iron and manganese（FeOOH and MnOOH） (Chapman, et al 1998). On the other hand, organic matters contained in water may result in a lower redox state of the sediments and overlying water column, which could cause dissolution of metal-containing mineral phases leading to the release of iron and manganese (MILLS, 1994). There is no deficit of iron and manganese in distribution system pipe lines raising the concern that these could be one of the major sinks. It is necessary to determine under what conditions these bound copper could be deposited on or dislodged from these sites.

Copper dosed into surface water showed the tendency of transformation of dissolved copper towards particulate forms. This transformation involves complexation by organic and inorganic ligands and transfer of dissolved copper towards colloidal and particulate forms (Elder, 1978). However, the forms, the rate and mechanism of copper transformation are still poorly understood. Eric & Philippe (Eric Van Hullebusch, 2003) have reported that NOM or humic substances attached to the sediments or inorganic particles can attract and bind copper to decrease the amount of copper available in bulk water phases. In distribution system pipes, there is no deficit of a surface for NOM or humic substances to bind. Probably this is the mechanism happening in the biofilms.

Dissolved organic carbon is regarded as an important ligand binding copper and form colloidal compounds in natural water bodies. According to Eric & Philippe's (2003) research, Cu was distributed among dissolved and colloidal ligands, roughly in proportion to organic carbon.

The stability of NOM-Cu complexes is reported to be quite strong at higher pH (8 or above) and weaker at lower pH although more complex binding sites are available on NOM to form complexes at lower pH (Takacs, et al., 1999). Cu-N bonds are reported to be more stable than Cu-O bonds in humic acids (Senesi, 1986). This implies that amines may form much stronger complexes. It is reported that nitrifiers can excrete organic compounds that lead to proliferation of heterotrophic micro-organisms (Mari T. T. Lipponen, 2002). These organic compounds can also increase the copper concentration in solution by forming NOM-Cu complexes.

In one study, Perdue (1985) showed that formation of inorganic Cu precipitates is much faster than that of NOM-Cu complexes formation leading to more precipitation happening closer to the point of addition.

In the distribution systems, pipe water is usually in contact with the wall surface that has a coating of $CaCO_3$ due to the saturated level of $CaCO_3$ in water. Water in distribution system is not in equilibrium with CO_2 in the air but in equilibrium with $CaCO_3$ deposited on the surface. Like samples drawn from distribution system, pH is expected to be lower and total alkalinity will be higher when the sample is put into a cylinder in an open system i.e. $CO_{2(g)}$ and $CO2_{(aq)}$ equilibrium is established. The removal rates are strongly dependent on the pH, water hardness and concentration of DOC (Elder, 1978). On the other hand, copper residence time in bulk water is dependent on colloidal fraction stability. Calcium ions can function as destabilising agents and help coagulation. Under this condition, metal bound copper and organic copper compounds can be quickly transported to sediments. This may be the reason leading to dramatic deposition of copper in distribution systems.

In summary, the literature review gives the following hints and concepts:

1. Copper hydroxide solubility may not be the controlling mechanism in drinking water system.
2. Copper hydroxide formed in bulk water may not be filtered by a 0.45μm membrane.
3. Copper-NH_3 complex formations could be neglected for initial investigation.
4. Inorganic copper forms precipitate much faster than it binds with NOM.
5. Copper-NOM bond is more stable at a higher pH although at a lower pH there are more binding sites (ionized carboxylic acid group) for copper to bind.
6. The pH of water is a very important variable that needs to be taken into account.
7. Copper can attach to suspended solids and particles which may contain metal-binding sites.
8. Copper can bind with iron, manganese etc. On the other hand, a lower redox status caused by organic matters may re-dissolve copper from metal-binding phases back into bulk water.
9. Copper can form complexes with inorganic species that could increase the copper concentration in solution to 60-70ug/L.
10. Copper-N bonds in Cu-NOM complexes are much more stable than Cu-O bonds.
11. What is precipitated in the pipe surface is more likely to be CuO than $Cu(OH)_2$.
12. Copper can bind with biofilms.
13. DOC is considered an important ligand binding copper and forms colloids.
14. Water in a distribution system is not in equilibrium with CO_2 in the air but in equilibrium with $CaCO_3$ deposited on the surface. Meanwhile, calcium ions could help transport copper binding compounds or particles quickly into sediments.

CHAPTER 3

SAMPLE MANAGEMENT AND METHODOLOGY OF COPPER ANALYSIS

3.1 Sample Sources, Collection and Preservation

3.1.1 Description of the Studied System

The Goldfields and Agricultural Water Supply System (G&AWSS, Figure3.1), is perhaps the world's largest water distribution system. The pipeline was commissioned in 1896 and was completed in 1903. This was primarily constructed to deliver water to the communities that had rapidly grown due to a gold rush in Western Australia's "Eastern Goldfields", such as Coolgardie and Kalgoorlie. The pipeline connects Mundaring Weir, near Perth, Western Australia, with the Mount Charlotte Reservoir at Kalgoorlie, 530 km (330 miles) away. It also serves towns further inland via extensions to the north and the south. The Mundaring Weir is fed with water from the Helena River in the Darling Scarp and has also been augmented with treated groundwater in recent years. It continues to operate, supplying water to over 100,000 people and more than six million sheep in 33,000 households, mines, farms and other enterprises.

Nitrification is known as one of critical causes accelerating chloramine decay along the distribution system. Especially in summer, pipes on the ground experience high temperatures (up to 50^{o}C), which is reported to be contributing to accelerating both chloramine decomposition and nitrifying decay. After several failed attempts to control nitrification in the system, copper inhibition was successfully trialled in the laboratory. This success led to a pilot trial in Merredin reservoir. This revealed that copper could be maintained in bulk water and up to 250 µg copper/L is necessary to control nitrifying bacterial activity (as measured by MPN method) in biofilms developed in artificially introduced attached mediums. Following the successful trial in the reservoir, another trial has been operating over the last 17 months in the C-K extension starting from

Cunderdin reservoir, one of several reservoirs in the main pipe of this system. Although, copper controlled nitrification (i.e. ammonia was preserved) in this trial, for the first time unexpected loss of copper from the bulk water for the whole of the trial period was observed. Data from the latter trial was used and has been analysed in this thesis, along with lab based experimental investigations to understand the fate of copper in the distribution system.

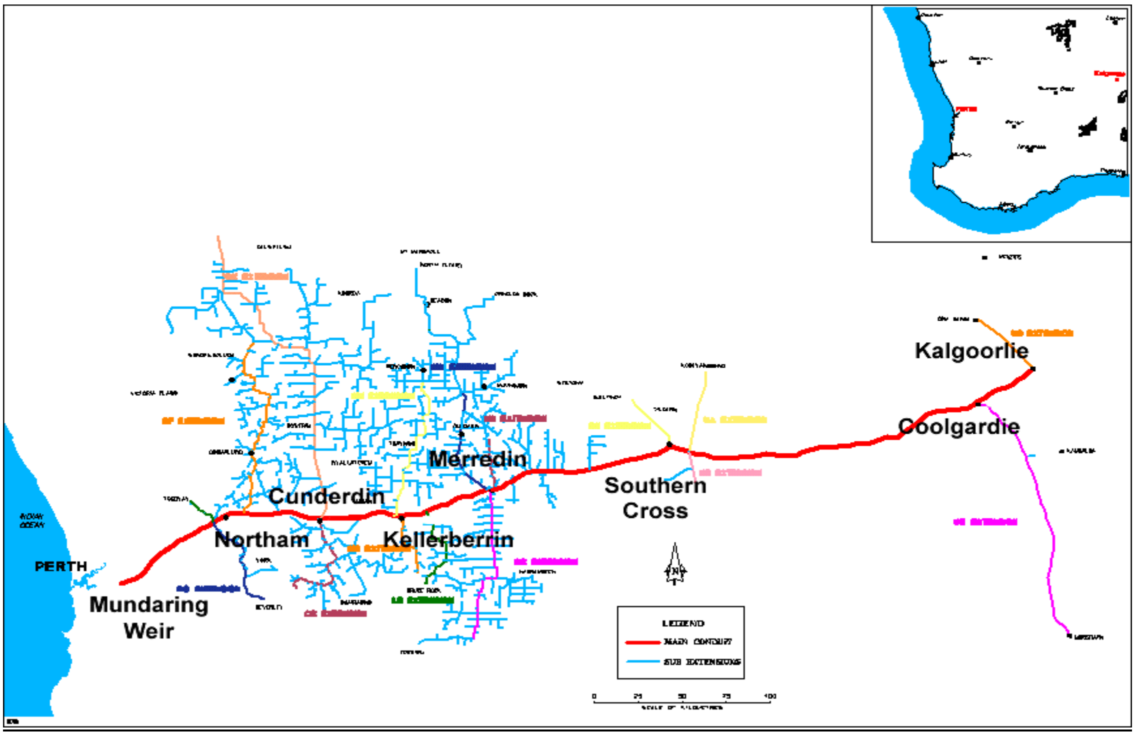


Figure 3.1 Map of G&AWSS System (Provided by Paul Nolan, Water Corporation, WA)

3.1.2 Sample Collection, Storage and Preservation

Most water samples used in the laboratory experiments were obtained from the outlet of Mundaring reservoir ahead of the chloramination point at which both ammonia and chlorine were dosed simultaneously. Sediments were regularly collected from CK extension pipelines where pilot copper dose trials have been undertaken. Water containing nitrifying bacteria was also drawn from some parts of C-K extension reticulation, running from Cunderdin reservoir to Merredin reservoir (58km) where nitrification was detected. Before sample collection in the field, containers were rinsed thoroughly three times with water having a chlorine concentration of 10-20 mg/L and then rinsed with sample water five to ten times to make sure the containers were free from contamination of other substances and bacterial species. Collected samples were transported to the laboratory without refrigeration and temperature at a around room temperature of 23°C.

Samples for ongoing experiments were normally stored in plastic jars with covers. All the stand-by samples were preserved under room temperatures (10~30°C) and were intact except for sampling and analysis.

Table 3.1 The History and Details of Sample Collection During the Research

Date	Site of sample collection	Purpose
January 2007	Outlet of Mundaring dam after Chloramination	"Mixing speeds" and "pH" experiments (Chapter 4.2)
April 2007	Outlet of Mundaring dam before Chloramination	0.2μm PC membrane filtration (Chapter 4.3)
June 2007	Outlet of Mundaring dam before Chloramination	GF filtration experiments (Chapter 4.4)
July 2007	Outlet of Mundaring dam before Chloramination	Induced aggregation experiments (Chapter 4.5)
September 2007	Historical data of C-K extension, offered by Water Corp	Sediments analysis (Chapter 5)

3.2 Methodology of Copper Analysis

3.2.1 The Principle of Copper Dosage

Australian Drinking Water Guidelines (ADWG) recommends copper levels of 2 mg/L, based on health considerations. Based on aesthetic considerations, copper in drinking water is recommended to not exceed 1mg/L. Complying with these guidelines and review of the experimental results obtained from Water Corporation studies by Department of Public Health officials led to the approval of 0.25mg/L as the dose level. Therefore, in this thesis 0.25 mg-Cu/L had been chosen as the dosing concentration in laboratory experiments. This has been the concentration in all pilot trials in parts of distribution systems except for the last few months when 0.4 mg/L was applied following revised approval from the Department of Public Health.

3.2.2 The Preparation of Cupric Sulphate Standard Solution

As an initial trial, copper sulphate was used in all copper dosing experiments. As mentioned previously, 0.25mg-Cu/L was the target concentration in all experiments. Standard copper sulphate solution (0.25g/L as Cu) was prepared in the water laboratory of Curtin University of Technology by mixing $CuSO_4$•$5H_2O$ into deionised water. The pH of the standard solution was maintained at 5.81 so all copper could be maintained as cupric ions. The volume of bulk water samples in all experiments ranged from 1.5~2.0 litres, consequently a 1.5~2.0ml standard solution was dosed by volumetric pipettes (20µl~1000µl) to each sample to make a target concentration of 0.25mg/L. The relative change of sample volume was therefore within 0.1%. Other details related to copper dosing (mixing speed, mixing time…etc), sampling procedures and chemical preparations are specific to each experiment and are discussed in respective sections.

3.2.3 Copper Measurement Method

Copper concentration analysis was mostly done by spectrophotometer (HACH DR2800). Bicinchoninate method (high range) and Porphyrin method (low range) were applied in the laboratory. Measuring ranges of the two methods are 0.04~5mg/L and 1~210µg/L respectively. Samples were digested by nitric acid (1:1) to pH 4~6 for total copper measurement. Potable pH meters with temperature compensation and a PC Multidirect photometer (Lovibond) were used to measure pH values. Some samples were analysed in SGS Australia Pty Ltd laboratory for comparison and confirmation of lab testing accuracy. ICP (inductive coupled plasma) spectroscopy was the procedure adopted in SGS for total copper analysis. For measuring dissolved copper concentration, filtration through 0.2µm PC (polycarbonate) membrane was processed before dissolved copper measurement. In order to minimise interaction between the sample and membrane and to prevent speciation changes, the volume of the filtrate was chosen to represent approximately 50% of the volume of the raw sample (Eric Van Hullebusch, 2003).

Other methods such as acid/base standard solutions, pH modification, coagulation and filtration, etc are detailed in each specific experiment.

CHAPTER 4

FATE OF COPPER IN BULK WATER

4.1. Introduction

4.1.1 The Fate of Copper in Natural Water

Generally, in natural water, copper exists in different forms: particulates (sediments or suspended solids), which could be $Cu(OH)_2$ or aggregates; colloids (tenorite, for instance, CuO); soluble copper (Cu^{2+}, inorganic or organic copper compounds, for instance, $CuCO_3^o$, $CuOH^-$, Cu-NOM).

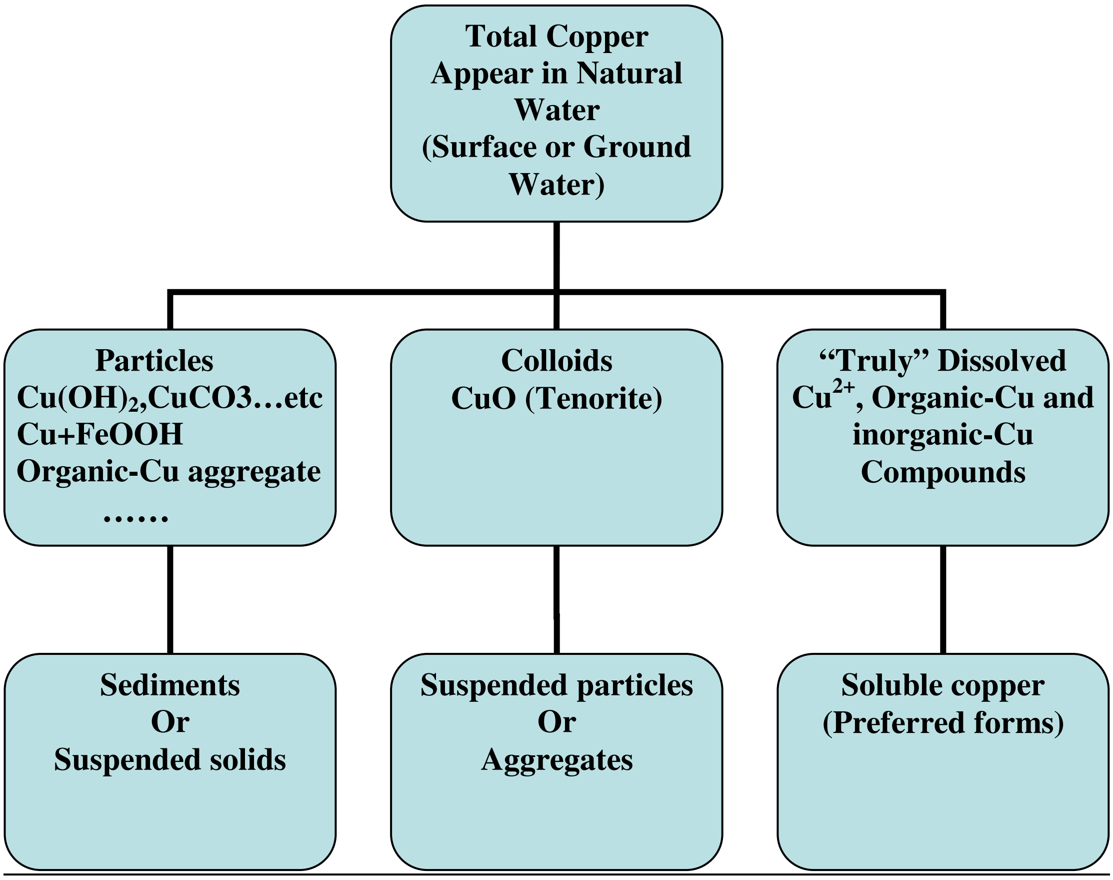


Figure 4.1 Integrated map of different forms of copper in natural water

Free cupric ions can hardly be found in natural water bodies (Vashnavi Sarathy, 2005). The dominated forms of copper or copper compounds are controlled by many aqueous factors. In pure water (ideally composed of H_2O, H^+ and OH^-) at pH around 8, copper exists mostly as sediments or suspended particles of $Cu(OH)_2$. This is simply controlled by solubility product of $Cu(OH)_2$ (Vernon L. Snoeyink, 1980). However, most of the natural or drinking water usually contains minerals such as Fe, Mn, Ca and Mg…etc, which can attach to copper and aggregate into particles. Meanwhile, Natural water or drinking water could possibly be buffered by a carbonate system (CO_3^{2-}, HCO_3^-) (Snoeyink, 1980). Copper such a system could be in equilibrium with CuO rather than copper hydroxide. Inevitably, some organic matters (NOM) or bacteria are present in natural water bodies or even in drinking water system. Copper combines with these organic and inorganic ligands to form compounds. Consequently, the dominance of copper form(s) could be a function of the above variables.

4.1.2 Basic Mechanisms Related to the Fate of Copper and the Investigation Procedure

Based on the integrated "map" of copper forms, copper loss in a drinking water system can be summarised in two ways: natural settlements (for example, sediments of relatively large particles such as $Cu(OH)_2$ or aggregated sediments (Cu compounds+Fe or Cu compounds+Mn) and deposition or adsorption onto biofilm or wall surface which could be caused by the roughness of cement pipe surfaces.

These mechanisms were investigated in this research in which sedimentation and particle formation have been emphasised because of some practical difficulties on probing biofilm samples from a real distribution system. Sedimentation observation was undertaken in bulk water samples. Filtration using 0.45μm and 0.2μm polycarbonate membranes was used to separate particles. Glass fibre filtration was used to simulate adsorption onto wall or settled particles.

In the end, each mechanism leading to copper "disappearance" from the solution was estimated. The essential mechanisms contributing to the fate of copper were suggested and partly quantified.

4.1.3 Factors Considered in the Research

The fate of copper is controlled by various factors existing in bulk waters. In order to find out which factors could be critical or decisive in copper control in a distribution system, experiments were designed to explore possible factors one by one. The controlling factors studied were:

Mixing speed: It was thought that mixing speed while dosing copper could affect the species distribution.

pH: This was regarded as the key parameter that controls the distribution of copper species. While effect of pH was investigated for some samples most of the samples were investigated at or near pH 8 since the distribution system water pH was around pH 8.

Ammonia and chloramine: These chemicals are either present or added in water during disinfectant addition and might combine with copper to form complexes.

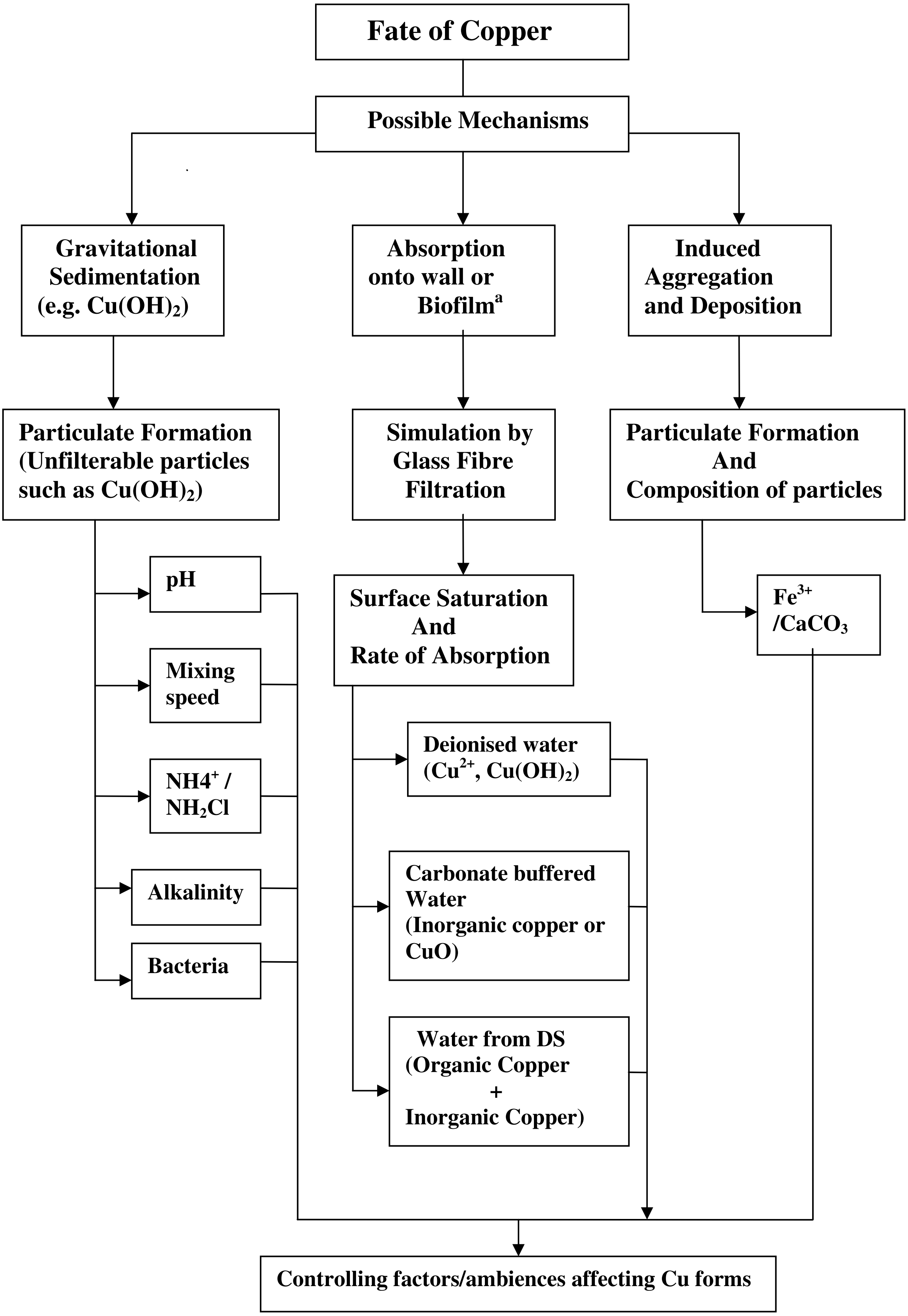
Alkalinity and carbonate: Copper solubility could be balanced by different forms (for instance, $CaCO_3$, CO_3^{2-} or HCO_3^-) in carbonate buffered water rather than in pure water.

Minerals: These are mainly Fe, Mn and Ca. They are possibly present in natural or drinking water system; the iron pipe used in Goldfield system could also release some mineral ions into the water

Dissolved organic matters (DOC): NOM are present in natural water bodies or in drinking water distribution systems. In addition, bacteria living in pipeline can produce extracellular compounds or cell biomass that itself could become NOM.

Bacteria: bacteria contained in the distribution system are considered having effects on the fate of copper.

Figure 4.2 Flowchart of "the Fate of Copper" Investigation Procedure



[a] biofilm impact had not been investigated.

4.2 Investigations on Gravitational Sedimentation

4.2.1 The Effect of Mixing Speeds

This experiment investigated whether different mixing speeds during copper dosage could affect the copper stability and dissolved copper concentration in bulk water. In other words, it would indicate if any copper particles (e.g. $Cu(OH)_2$) could form and settle down when there was possible uneven or weak mixing during copper dosing in the field.

Sample preparation and methodology

Chloraminated water drawn from the outlet of Mundaring dam was used in this experiment. Water samples were poured into four 2 litres plastic wide mouth jars. Subsequently, a cupric sulphate standard solution was added making copper dosage around 0.25-0.30mg/L as Cu. Jar tester was used for mixing at speeds of 20rpm, 40rpm, 80rpm and 160rpm were used to these bulk waters and the mixing time was set at 2 minutes for all samples. After the mixing protocol was implemented, all the samples were left intact at ambient room temperature for the next four days except for sampling for bulk water copper concentration without affecting the sedimentation process. Samples were drawn out from the point 1cm beneath the water surface in 2 litres jars for total copper concentration measurement. It's denoted "bulk [Cu]" in the following experiments.

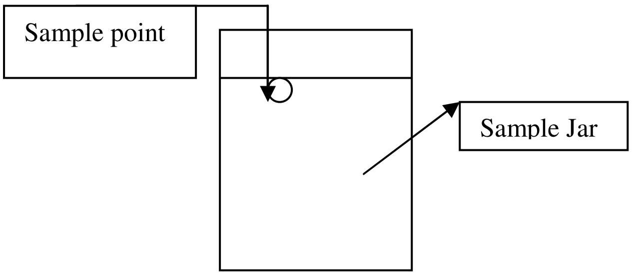


Figure 4.3 Method of Bulk Copper Concentration Measurement

Samples were drawn after one, two and four days respectively after the completion of the copper dosage. Total bulk copper concentrations were measured.

Results and Discussion

Table 4.1 Results of Bulk Copper Concentrations at Various Mixing Speeds

Mixing speeds (rpm)	Copper dosage (µg/L)	Bulk [Cu][1] (µg/L) during 4 days		
		1st day	2nd day	4th day
20	280	270	260	260
40	290	270	270	260
80	290	280	270	260
160	280	270	270	270

Bulk [Cu] [1]: The way drawing samples for bulk copper test is shown in Figure 4.3.

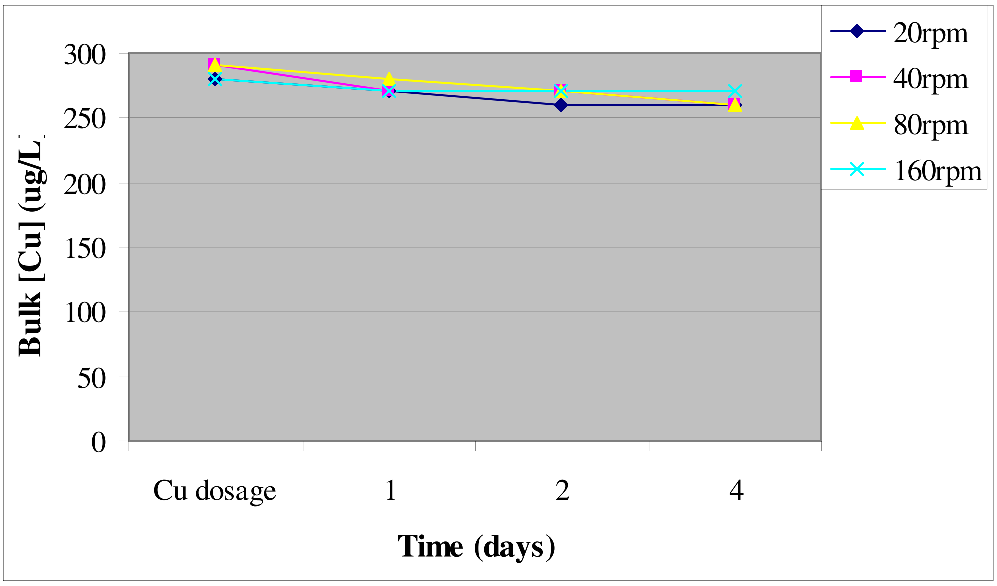


Figure 4.4 Bulk Copper Measurements at Various Mixing Speeds

ICP method was used for total copper measurement and analysed by SGS laboratory.

Discussion

Copper concentration had decreased from 280~290µg/L to 260~270µg/L on the fourth day (Figure 4.4). Results for different mixing speeds on a specific day were within

±10μg/L. The experimental error for measurement is ±10μg/L. These results did not show much difference from samples at different mixing speeds, although prolonged stagnation did show some sedimentation.

Conclusion

These results indicated that sedimentation did not take place in Mundaring water samples. As different mixing speeds did not show obvious difference in copper concentrations, it was concluded that mixing speeds did not have effect on copper concentration in bulk water and even poor mixing did not lead to sedimentation.

4.2.2 The Effects of pH

According to what was observed from the "mixing speed" experiment, sedimentation did not happen at pH 8 in Mundaring water samples. This result looked contradictory to what was reported in the literature, that only 3ug/L dissolved copper could exist in pure water at pH 8. As mentioned previously, natural water like that at Mundaring contains some substances that affect copper solubility. However, considering that pH is normally regarded as a key parameter for solubility of many mental ions, it is necessary to investigate whether and how different pH values affect Cu concentration and sedimentation in Mundaring water. The pH values ranged from 6.5 to 9.8 in this experiment covering the normal pH range of drinking water. In addition, a relatively high pH of 9.8 was selected as an "extreme" negative condition for copper solubility.

Sample preparation and methodology

Chloraminated water from the outlet of Mundaring dam was chosen in this experiment. The initial total chlorine of sample is 3.5mg/L, pH 8.0.

Water samples were stored in four identical 2-litre plastic bottles. Standard solutions H_2SO_4 (N/1) and NaOH (N/1) were used to adjust pH values of these samples to 6.56, 7.53, 8.65 and 9.80 respectively. A Potable pH meter with temperature compensation was used to measure pH values. PC Multidirect photometer (Lovibond) was also used to cross-check pH. A cupric sulphate solution (0.25g/L as copper) was added to each sample to make the concentration of all samples around 0.25mg/L as copper. All the water samples were left untouched at ambient temperature for the next ten days after copper dosing was completed. Bulk water in each bottle was drawn for analysis of total copper. (Refers to Figure 4.3 in this chapter for method) Total copper concentrations were measured by Inductively Coupled Plasma (ICP) Spectroscopy (This method was used by SGS Australia Pty Ltd to analyse total copper concentrations).

Results and Discussion

Table 4.2 Results of Bulk Copper Concentrations at various pH values

pH	**6.56**	**7.53**	**8.65**	**9.8**
Cu dosage (µg/L)	270	250	240	240
Bulk [Cu]^1 (µg/L)	230	220	190	210

Bulk [Cu]^1: water samples 1cm beneath the bulk water surface were drawn for total bulk water measurements (Figure 4.3) after 10 days.

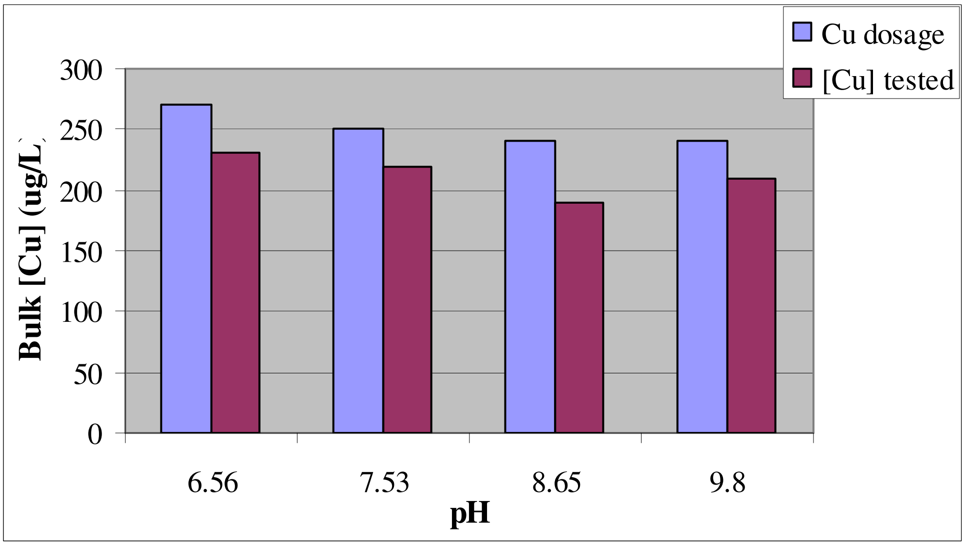


Figure 4.5 Bulk Copper Concentrations at Various pH Values

Discussion

The range of pH values (6.56 to 8.65) covers the normal pH range in drinking water. Figure 4.5 indicates that copper concentrations in bulk water decreased by only 30~50μg/L with this pH variation. Even relatively high pH (9.8) did not show substantial copper concentrations decrease. In addition, these results showed that copper solubility in Mundaring water does not conform to the normal solubility Vs pH relationship: the higher the pH, the lower the solubility, which is supposed to be present in "pure" water. The highest pH (9.8) only showed a 30μg/L decrease while a 40μg/l decrease of copper concentration took place in the lowest pH 6.56.

Conclusion

Although some sedimentation (30-40 μg/L) was noticed in 10 days, it was not substantial enough to account for the loss of almost all copper (250 μg/L) within just a few hours travel in the pipe lines. It indicates that this range of pH values have little effect on bulk water copper concentrations and sedimentation in Mundaring bulk water.

Solubility products of $Cu(OH)_2$, CuO and $CuCO_3$ are $10^{-18.7}$, $10^{-20.35}$ and $10^{-9.63}$ respectively. These solubility products may constrain soluble copper concentrations in Mundaring bulk water. However, it is possible that these copper particles could suspend in the bulk water instead of settling down. In order to separate particulate copper, the filtration experiments need to be done.

4.3 Separation of Filterable Particles from Bulk Water: 0.2μm Polycarbonate (PC) Membrane Filtration

4.3.1 The Purpose of Filtration Experiments

The results of the "mixing speed" experiment and pH experiments indicated that there was almost no gravitational sedimentation and no substantial effect from different pHs or different stirring speeds. Instead of settling down, copper particles or any insoluble copper might stay suspended in bulk water. In the distribution system, these copper particles could possibly be deposited to the pipe surface or sediments in pipelines. On the other hand, they might be absorbed to biofilm attached to the surfaces of pipelines. If these particles such as $Cu(OH)_2$ did form in bulk water and remained suspended instead of settling down, they could be separated by filtration. A 0.45µm membrane is normally used to partition between suspended and dissolved copper. However, it is reported that $Cu(OH)_2$ particle size could vary with pHs and decrease with the decreasing pH (R.O.Skold, et. al., 2001). The curve is reproduced in Figure 4.7. Referring to the literature, average particle size of 385nm, $Cu(OH)_2$ particles therefore can not be filtered by a 0.45µm membrane. Consequently, a 0.2µm polycarbonate membrane was chosen. The particle size of CuO which could possibly form in carbonate buffered water (e.g. Mundaring water) is reported to be 30nm and therefore it can not be filtered by 0.2µm membranes. $CuCO_3$ has much higher solubility ($10^{-9.63}$) than $Cu(OH)_2(10^{-18.7})$. Without the presence of organic ligands and at pH 8 Cu^{2+} can only be present up to $10^{-6.6}$ M. At pH8, the dominating form is bicarbonate, although the alkalinity is about 100 mg/L. Hence, there is a little possibility that $CuCO_3$ will be formed in a water that is at pH8 and when alkalinity is about 50-100 mg/L. Thus the possibility of $CuCO_3$ particles formation in Mundaring water when carbonate alkalinity of Mundaring is around 100mg/L, pH is 8, and Cu dosage is 0.25mg-Cu/L is minimal. Nevertheless, it is possible that other inorganic bound copper particles including $CuCO_3$ might be trapped by 0.2µm membrane.

In order to find out which factors might control particulate formation or copper solubility, the following factors were considered in filtration experiments: Ammonia, chloramine, organic matters contained in Mundaring water, alkalinity (carbonate buffered system), and bacteria.

4.3.2 The Reason for the Selection of 0.2µm PC Membrane: Solubility and Particulate Size of $Cu(OH)_2$ as a Function of pH

The experiment was based on the fate of copper in deionised (“pure”) water, in which all sediments or particles are assumed to be copper hydroxide, which is controlled only by copper solubility products under specific pH values.

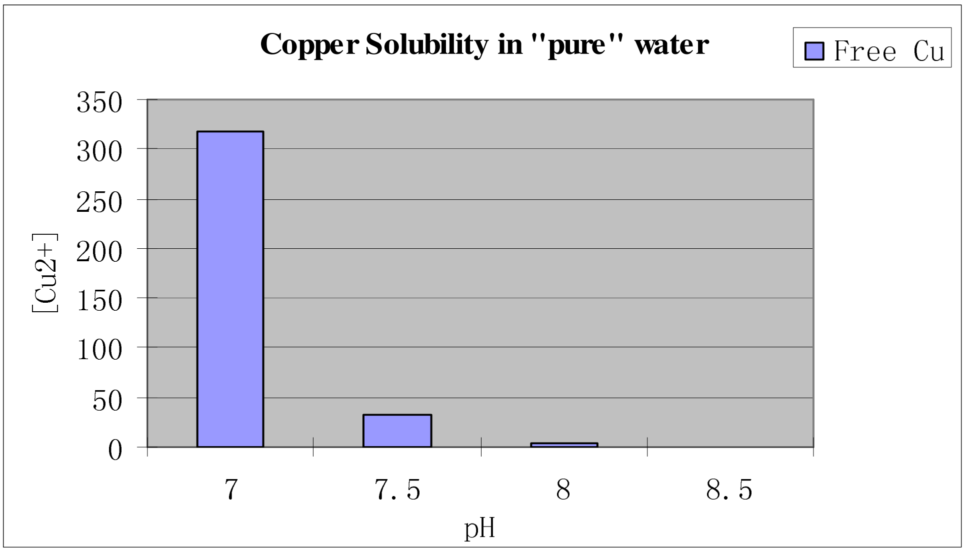


Figure 4.6 Theoretical Soluble Copper Concentrations at Various pH Values in "Pure" Water (Solubility product ($10^{-19.3}$) of $Cu(OH)_2$ is applied in the calculation)

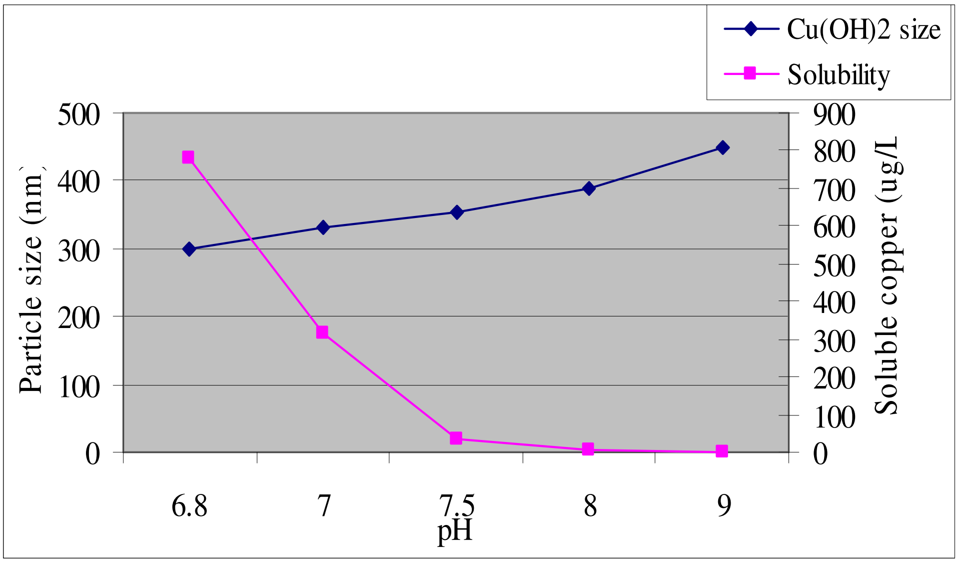


Figure 4.7 Theoretical Plot of $Cu(OH)_2$ Particle Size and Copper Solubility as Functions of pH Values in "Pure" Water

Discussion

Free copper concentration as determined in "pure" water at different pH values is shown in Figure 4.6. There are almost no free cupric ions in bulk water at pH 8.0 (which is a typical pH in Mundaring water sample and in the distribution system) provided that cupric ions concentration is controlled by the solubility product of copper hydroxide:

$Cu^{2+} + 2OH^{-} \rightarrow Cu(OH)_{2(s)}$ $[Cu^{2+}]\bullet[OH^{-}]^{2} = 10^{-19.3}$

Figure 4.7 demonstrates that the particle size of copper hydroxide in "pure" water is positively correlated to pH values. When pH increases from 6.8 to 9.0 (typical pH range in drinking water), the particle size of $Cu(OH)_2$ increases from 300nm to 450nm. A 0.45µm membrane normally used in particle filtration, is not suitable in $Cu(OH)_2$ particulate separation at pH 8.0 (normal pH of Mundaring water samples and bulk water in the distribution system) because the particle size is less than 400nm at this pH. Instead, a 0.2µm polycarbonate (PC) membrane was chosen to separate copper hydroxide at targeted pH values in this research. In addition, the filtration of copper hydroxide from deionised water using 0.2um and 0.45um membranes were undertaken in the laboratory experiments and confirmed this theory (Appendix B)

4.3.3 0.2µm PC Membrane Filtration Experiment

In the course of the following series of experiments, a 0.2µm PC membrane was used to trap any copper hydroxide particles formed and suspended in Mundaring water. From the results of previous experiments, the possible effects from pH and mixing speed had been excluded.

However, some chemicals and compounds in natural water could still combine with copper or release it from a particulate state. Ammonia and chlorine are dosed into distribution system for disinfection purpose. Ammonia is known as a ligand which can complex with copper and form soluble copper-ammonia complexes. Copper could also combine with organic matter in the water and could form organo-Cu compounds. On the other hand, water in the distribution system is most probably buffered by a carbonate system ($CaCO_{3(s)}$, CO_3^{2-}, and HCO_3^{-}). In carbonate buffered solution, copper solubility is balanced by $CuO_{(s)}$ (solubility product: $10^{-20.35}$) rather than $Cu(OH)_2$ ($10^{-19.3}$) (Snoeyink, 1980). Under these circumstances and pH in a range of 6.5-9.5 (covering the pH range of drinking water), major copper related particles should be CuO (Vernon L. Snoeyink, 1980). Meanwhile, dissolved copper forms would be inorganic-Cu ($CuCO_3^{o}$, $CuOH^{-}$…) and organo-Cu complexes rather than free cupric ions (Snoeyink, 1980). The average particle size of CuO is 30nm. If these fine particles are formed in

Mundaring water, a 0.2µm PC membrane is not able to filter them. Furthermore, bacteria or bacterial products in bulk water could possibly combine with copper and form soluble compounds.

Generally, the controlling factors mentioned above were set in deionised water and Mundaring water in this filtration experiment. The results were expected to indicate in which circumstances major copper species are filterable particulate forms. It would give a further understanding of the possibility of particulate formation such as $Cu(OH)_2$ under various conditions.

Sample preparation and methodology

Table 4.3 Description of Mundaring Water Samples in 0.2µm Filtration

Samples labels	pH	Alkalinity (mg/L as CaCO3)	Total Cl2 (mg/L)	NH3-N (mg/L)	UV Abs	Absence of bacteria
MWR	8.05	76	0	0	0.45	N/A
MWA	8.05	65	0	0.5	N/A	N/A
MWC	8.05	70	2.0	0.5	N/A	N/A
MWR-DOC[1]	8.0	50	0	0	0.18	N/A
MWR-B[1]	8.0	N/A	0	0	N/A	Yes

MWR-DOC[1]: $FeCl_3$ was used for coagulation and flocculation and the filtrate after GF filters was named as MWR-DOC sample. Most of the coagulable DOC and NOM had been removed after this process. UV (254nm) absorbance of MWR and MWR-DOC were found to be 0.45 and 0.18 respectively (100mm glossary quarts sample cell was used in UV measurements). This showed that about 60% of the NOM is removed. Kastl et al., 2003 showed that in natural surface waters organic carbon which is removable by coagulation was between 50-80%, the majority of the values at 65%. It can therefore be concluded that 20 mg/L $FeCl_3$ in the sample had removed most of the coagulable organic carbon.

MWR-B[1]: MWR was filtered by a 0.2µm PC membrane. The filtrate was MWR-B.

Table 4.4 Description of Deionised Water Samples in 0.2μm Filtration

Samples labels	**pH**	**Alkalinity (mg/L as CaCO3)**	**$CaCO_3$ dosage (mg/L)**	**Na_2CO_3 dosage (mg/L)**
DW	5.8	N/A	0	0
DWH[1]	8.1	N/A	0	0
DWHNa	8.1	57	0	100
DWHCa	8.1	49	100	0

Samples labels	**pH**	**Ammonia dosage (mg/L)**	**Chlorine dosage (mg/L)**
DWHA	8.05	0.5	0
DWHC	7.9	0	2
DWH(C+A)	8.05	0.5	2

DWH[1]: The dominating copper form in deionised water at pH 8.1 is $Cu(OH)_2$.

(1) MWR, MWA, MWC, DWHA, DWHC and DWH(C+A): the effect of ammonia and chloramine

Mundaring raw water (MWR) was drawn from the outlet of Mundaring dam ahead of chloramination point. Ammonium chloride (NH_4Cl) standard solution (1g/L as NH_3-N) and sodium hypochlorite (NaOCl) standard solution (1g/L as Cl_2) had been prepared. An NH_4Cl standard solution was dosed into Mundaring water sample to make MWA. NH_3-N concentration of 0.5mg/L in MWA was considered to be the typical concentration in distribution system, although 0.8mg-N/L is dosed at Mundaring. Monochloramine solution had been made by mixing NH_4Cl and NaOCl solutions. The weight ratio of NH_3-N to Cl_2 was 1 to 4. Monochloramine was added into Mundaring water sample to make MWC, in which the initial total chlorine concentration was made at 2mg/L. Chlorine and ammonia concentration was tested by spectrophotometer (HACH DR2800). Experiments concerned with MWR, MWA and MWC were expected to show how ammonia or chloramine could affect the formation of filterable particles and the fate of copper in Mundaring water. Meanwhile, a similar ammonia and chlorine dosing procedure was undertaken in deionised water instead of Mundaring water to make DWHA, DWHC and DWH (C+A). Experiments concerned with DWHA, DWHC and DWH (C+A) were expected to show how ammonia and chloramine can affect copper solubility in “pure” water.

(2) MWR-DOC: the effect of dissolved organic matters

Ferric chloride, widely used in water utilities as a coagulant was used to remove most of the dissolved organic carbon (DOC) from Mundaring water. The concentration of $FeCl_3$ was 20mg/L. A jar tester was used to coagulate and flocculate $FeCl_3$ in Mundaring water. Initially during coagulation, a 200rpm mixing speed was set for 2mins. In the flocculation phase, a 20rpm mixing speed was maintained for 20mins. The pH of coagulation and flocculation process was controlled at around 6.5. After the process had been completed (Referring to 2.2.2 Chapter 4, for pH modification methods), standard acid/base solutions were used to increase the pH of MWR-DOC back to 8.05. UV absorbance (254nm, 100mm glossary quarts sample cell) values of MWR and MWR-DOC were measured as indicators of DOC. UV absorbance of MWR was 0.45 while that of MWR-DOC was 0.18. UV measurements were performed using UV-visible spectrophotometer (Helios Alpha, Beta, Gamma, Delta UV1, Aquamate, Biomate). If organo-Cu complexes were the mechanism leading to soluble copper, MWR-DOC were expected to show less dissolved copper than MWR did.

(3) MWR-B: the effects of bacteria and suspended solids

The effects of bacteria and suspended solids in Mundaring water on copper solubility are unknown. In order to investigate how bacteria and suspended solids are contributing to the fate of copper (soluble vs filterable), Mundaring water was filtered using a 0.2μm PC membrane. The filtrate was dosed with copper to see if bacteria and suspended solids could impact the fate of copper.

(4) DWHCa and DWHNa: the effect of alkalinity and carbonate buffered system

$CaCO_3$ and Na_2CO_3 powder was added to deionised water respectively to make carbonate buffered solution named DWHCa and DWHNa. The dosage of both $CaCO_3$ and Na_2CO_3 was 100mg/L. After dosing, pH values of both samples were modified to 8.1 by sulphurous acid standard solution (1N). A PC Multidirect photometer (Lovibond) was used to measure pH and total alkalinity (bromcresol tablets were used to measure total alkalinity). The results of DWHCa and DWHNa filtration were expected to indicate how a buffered solution and a $CaCO_3$-equilibrium system could affect the formation of filterable particles.

(5) DW and DWH: Proof of copper hydroxide sedimentation in pure water

Deionised water with high and low pH values had been prepared respectively. Both of these samples were used to prove $Cu(OH)_2$ does form particles in deionised water, as reported in literature. Meanwhile, the results from DW and DWH would allow a comparison of the results achieved from the other samples.

With reference to Chapter 3 for copper dosage and total copper analysis methodology, after samples preparation was completed, they were left intact in the ambient room temperature for the next three days except for the sampling of bulk water concentration analysis and filtration.

Results and discussion

Table 4.5 Results of 0.2μm PC Membrane Filtration

Sample label	Cu Dosage (μg/L)	[Cu] in Filtrate (μg/L) [1]	Cu Blocked (μg)
DW	250	250	0
DWHA	250	12	238
DWHC	270	11	259
DWH (C+A)	250	12	238
DWH	250	7	243
DWHNa	250	200	50
DWHCa	240	150	90
MWR	250	240	10
MWR-DOC	250	170	80
MWA	260	240	20
MWC	250	230	20
MWR-B	250	240	10

Note: one litre of each sample was filtered by 0.2μm PC membrane (47mm).

[Cu] in Filtrate (μg/L) [1]: total copper concentration in filtrate. Before total copper measurement, samples were digested by nitric acid (1:1) to a range of pH 4-6.

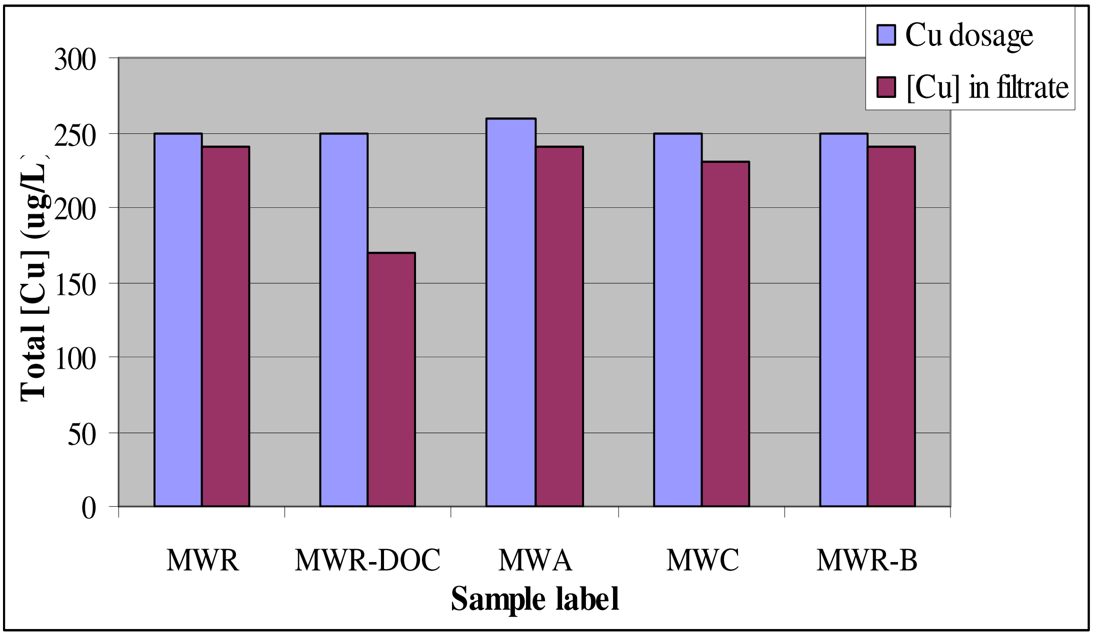


Figure 4.8 The Effects on Particle Formation of Ammonia, Chloramine, Dissolved Organic Carbon and Filterable Solids (bacteria/suspended solids)

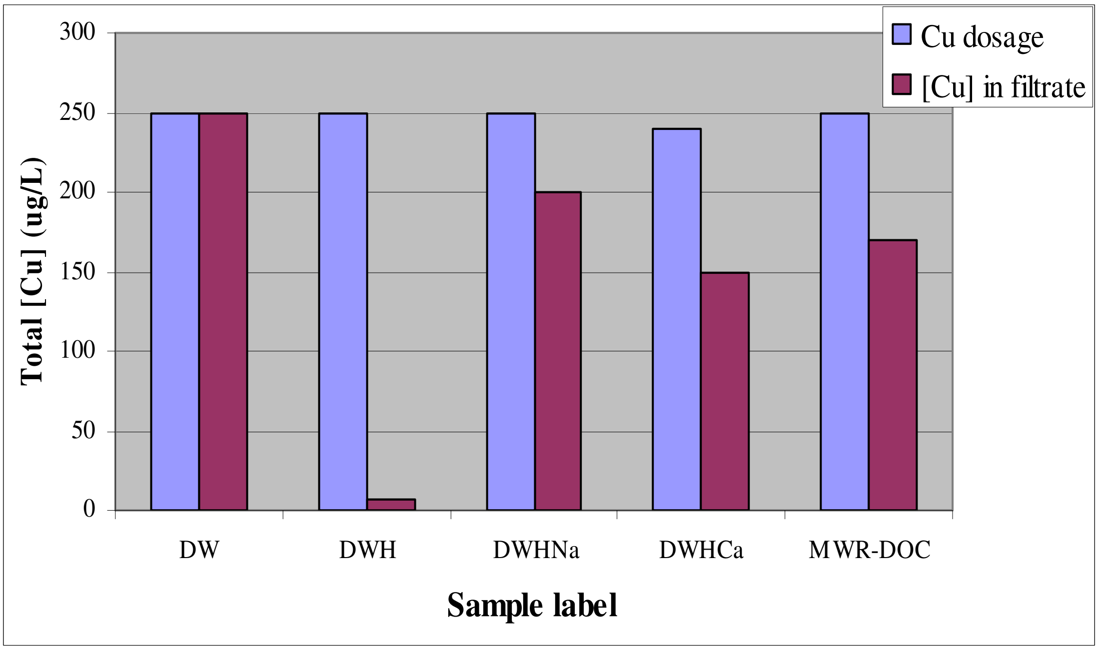


Figure 4.9 Copper Concentrations in Deionised Water or Carbonate Buffered Solution

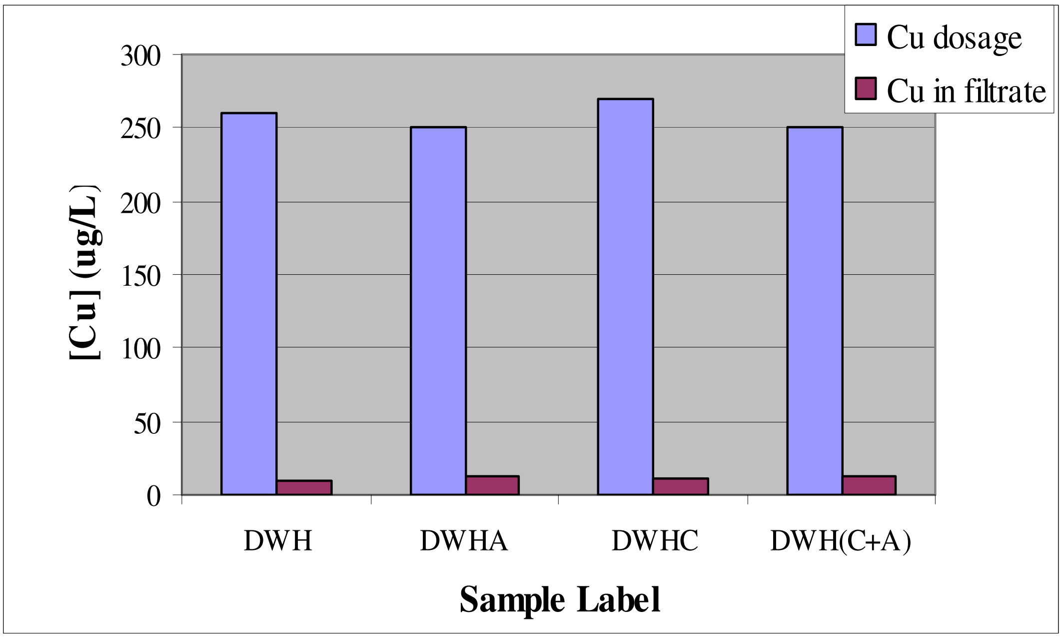


Figure 4.10 Copper Concentrations in Deionised Water Containing Ammonia, Chlorine or Chloramine

Discussion

As shown in Figure 4.10, only 11~12ug/L copper was found in the filtrate of those four deionised water samples (DWH, DWHA, DWHC and DWH (C+A)). These results indicated that 95%~96% of total copper in these solutions had formed $Cu(OH)_2$ and been filtered out. After adding ammonia, chlorine or chloramine, the solubility of free copper in bulk water did not increase. Figure 4.8 shows MWR, MWC, MWA and MWR-B showed similar copper concentrations of 230 to 240µg/L in the filtrate (10µg/L discrepancy was within instrument errors). Only 10ug/L copper in the filtrate of Mundaring raw water (MWR) and MWR-B respectively indicated that dissolved copper concentration remained high without ammonia, chlormine or suspended solids/removable bacteria being present in Mundaring water.

On the other hand, only 170ug/L out of 250ug/L was found in the filtrate of MWR-DOC sample (Figure 4.9). After 20mg/L ferric chloride coagulation, roughly 60% of DOC in Mundaring water had been removed (UV absorbance (254nm, 100mm sample cell) was 0.45 for MWR and 0.18 for MWR-DOC) from MWR sample. Probably this 60% organic carbon removed by enhanced coagulation could complex with that 70µg/L

(240μg/L-170μg/L) of copper which can not be filtered by 0.2μm PC membrane. Meanwhile, Figure 4.9 also showed that 150μg/L copper was found in the filtrate of DWHCa. . Compared with 170μg/L copper in MWR-DOC (partly DOC removed), it indicates that MWR-DOC sample could be regarded as a calcium carbonate buffered solution and 20ug/L more copper was found in MWR-DOC than that in DWHCa. This might be brought by DOC left in MWR-DOC sample which can not be removed by coagulation.

Only 7ug/L copper in the filtrate of DWH confirmed that $Cu(OH)_2$ does form and dominate in "pure water" at pH 8.1 and can be filtered by a 0.2μm membrane (Figure 4.9). When deionised water was buffered by calcium carbonate (DWHCa), copper concentration in the filtrate increased to 150μg/L. It indicated that copper may combine with inorganic ions to form inorganic copper compounds ($CuCO_3^o$, $Cu(OH)^{3-}$) or tenorite CuO (the particle size of CuO is only 30nm, so it can not be filtered by 0.2μm membrane) (Vernon L. Snoeyink et al., 1980). The reason DWHNa (sodium carbonate buffered solution) showed 50μg/L more copper in the filtrate than DWHCa was not clear. Probably $CaCO_3$ formed in DWHCa could help aggregate copper particles. This might have helped in removing about 50μg-Cu/L.

Conclusions

In deionised water at pH 8.1, the dominating copper form is $Cu(OH)_2$ particles which can be filtered by a 0.2μm PC membrane.

Ammonia and chloramine hardly increase copper solubility in deionised water. In addition, up to 0.5mg-NH_3-N/L and 2mg-Cl_2/L, which exist in the distribution system, have little effect on fate of copper in bulk water. Filterable bacteria or suspended solids in Mundaring water can not affect the fate of copper.

The equilibrium balanced by $Cu(OH)_2$ is not the controlling mechanism in carbonate buffered water at pH 8. Inorganic copper compounds and tenorite may form in carbonated buffered solutions and increase copper concentrations in bulk water. Both inorganic and organic copper compounds may contribute to relatively high dissolve copper concentrations in Mundaring water.

In terms of the results achieved in this experiment, copper species in Mundaring water can be roughly identified and quantified (Figure 4.11).

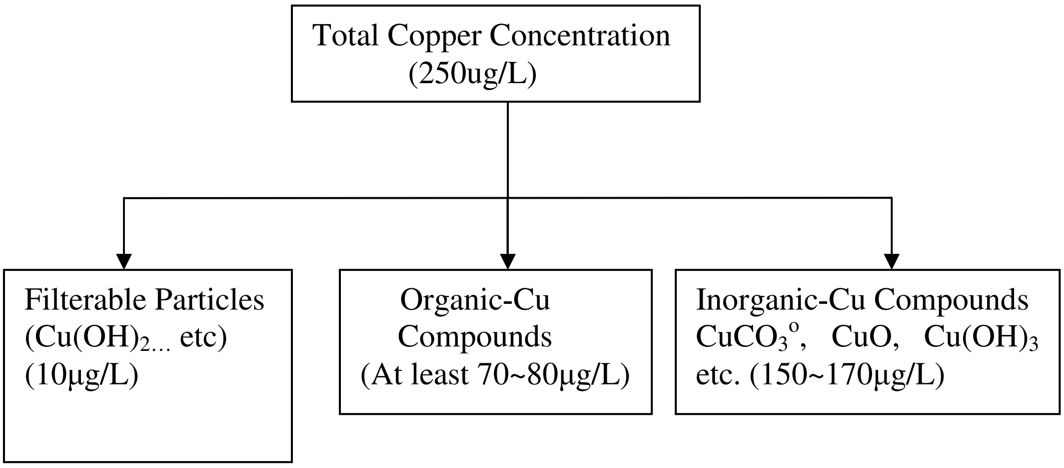


Figure 4.11 Compositions of Total Copper Species in Mundaring Water

4.4 An Investigation on Surface Adsorption: Glass Fibre (GF) Filtration Experiments

The previous study confirmed two basic points:

1. Gravitational sedimentation could be neglected in Mundaring bulk water without considering other factors from the distribution system.
2. $Cu(OH)_2$ particles hardly form in Mundaring water (only 10μg/L).

Instead, copper species exist in Mundaring water might have formed at following concentrations:
Dissolved organo-Cu complexes (70~80μg/L)
Inorganic-Cu compounds (150~170μg/L)
CuO fine particles in carbonate buffered system.

The first point excludes the possibility of natural sedimentation in Mundaring water. However, copper may "disappear" in two other ways: surface/biofilm absorption and induced aggregation and deposition. The rough inner cement surface of a pipeline provides a tremendous area to which Cu-containing particles and even some dissolved substances could attach or adsorb. On the other hand, some mineral ions such as Fe^{3+}, Mn^{2+} and Ca^{2+} introduced to or released from distribution system could induce aggregation of copper particles.

The second point indicates the possible major forms that copper can exist in Mundaring bulk water. Having understood the major copper species in chloraminated and unchloraminated Mundaring water, in this section, answers to the following questions are sought:

- Could all of these copper species be adsorbed to the pipe surface?
- Does pipe surface have different ability to adsorb different copper species?
- What is the adsorptive capacity to copper species in Mundaring water?

Although real pipe modelling was not feasible within the period of this research, glass fibre filters were used to simulate the pipe surface. Glass fibre filters for qualitative analysis had been capable of adsorbing copper particles and even soluble copper in preliminary laboratory GF filtration experiments (Appendix C). Subsequently, GF filtration was used to simulate the surface/wall adsorption mechanism. Although the compositions of the surface of the real pipe is much more complicated than those of GF filters, simulating adsorption by GF filters may still provide a partial understanding of adsorption mechanism itself, even if quantifying the possible real adsorption in the distribution system by GF adsorption experiments is not appropriate. Consequently, GF filtration could be regarded as a threshold of investigating adsorption phenomenon. Samples were filtered by MN1674 GF filters (containing ash, qualitative filter paper). Amount of copper adsorbed by filters was estimated.

Sample preparation

Table 4.6 Description of Water Samples in GF Filtration

Sample labels	pH	Alkalinity (mg/L as CaCO3)	CaCO$_3$ dosage (mg/L)	Na$_2$CO$_3$ dosage (mg/L)	UV Abs
MWR	8.05	76	0	0	0.45
MWRL	5.8	N/A	0	0	N/A
DWNa	8.1	57	0	100	N/A
MWR-DOC	8.05	50	0	0	0.18
DW	5.8	N/A	0		N/A
DWCa	8.0	49	100	0	N/A

Procedures of sample preparation were described in 3.3 of this chapter. Filtration methodology is detailed in each of the following sections.

4.4.1 Repeated GF Filtration

The following filtration procedure was undertaken in this experiment: 300ml of each sample was filtered by one GF filter (MN1674, 47mm, ashes contained). Each filtration was repeated through the same filter until copper concentration in the filtrate ceased to decrease. Samples described above were expected to have specific dominant copper species. Final copper concentrations in filtrates of different samples could indicate the different ability of the GF filter to absorb different copper species.

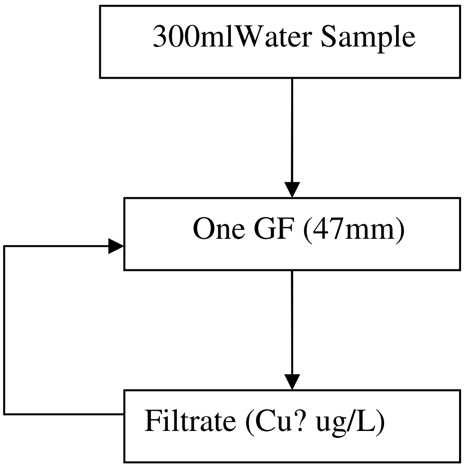


Figure 4.12: Flowchart of Repeated GF Filtration Procedure

Results and Discussion

Table 4.7 Results of Repeated Filtration by One GF Filter

		[Cu] in filtrate (µg/L)					
Sample label		**MWR**	**MWRL**	**DWNa**	**MW-DOC**	**DW**	**DWCa**
Cu dosage		240	250	250	270	280	240
Times of Filtration	1	190	220	140	160	85	120
	2	180	210	130	140	50	110
	3	180	190	120	120	20	90
	4	180	190	120	120	**20**[1]	90

20[1]: 20ug/L measured in DW is the lowest testing limit of the instrument

300ml of each sample was used in this experiment.

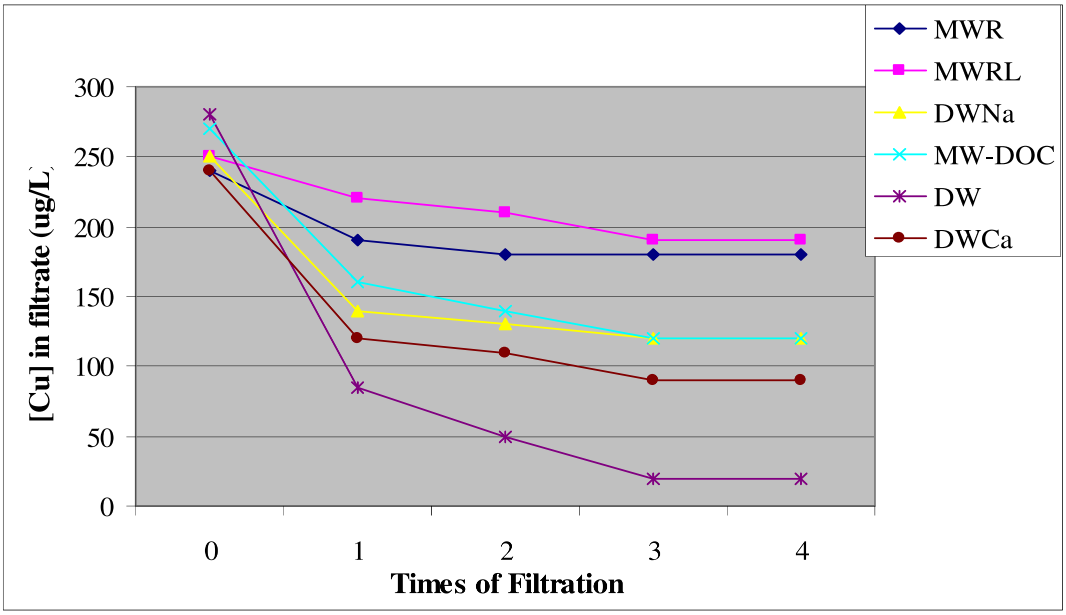


Figure 4.13 Cu Concentrations Vs Time of Filtration during Repeated GF Filtration

"0" in "times of filtration" axis corresponded to Cu dosage concentration

Discussion

Figure 4.13 indicates the different ability of GF filters to absorb different copper species. The ability of GF absorption showed the following sequence:

DW> DWCa > MWR-DOC = DWNa > MWR ≈ MWRL

GF filters demonstrated the strongest ability to absorb Cu^{2+} (DW), only 20µg/L Cu was left in the end (maybe less, considering 20µg/L is the lowest limit for the instrument). On the other hand, still 180µg/L Cu was left in Mundaring water, the second highest concentration achieved among all samples.

MWRL showed a similar trend as MWR (Figure 4.13) and almost the same final concentration (190µg/L Vs 180µg/L, 10ug/L can be neglected as instrument errors). It indicates that Cu^{2+} was not released from copper compounds in Mundaring water even at a low pH of 5.8, or else it would conform to the trend of DW.

The similar results achieved from DWCa, DWNa and MWR-DOC reassured that inorganic copper compounds and CuO contribute to the fate of copper in Mundaring water. The small difference of Cu concentrations (120-90=30µg/L) between DWCa and MWR-DOC is probably caused by parts of organic copper compounds remaining in MWR-DOC. Similarly, it could be concluded that organic matter coagulated by ferric hydroxide is responsible for organic matter complexation with copper.

Conclusion

A GF filter has obviously different abilities to absorb different copper speces. It has strongest ability to absorb free cupric ions. On the other hand, organic copper compounds in Mundaring water demonstrated relatively strongest ability against GF absorption. The GF filter's ability to absorb inorganic copper compounds and tenorite is stronger than organic copper compounds but weaker than Cu^{2+}. Similarly, it could be concluded that organic matter coagulated by ferric hydroxide is responsible for organic matter complexation with copper.

4.4.2 Successive GF Filtration

In terms of the results achieved in "repeated filtration", all the Cu-containing species, including organic copper compounds, inorganic copper compounds and probably the tenorite (CuO), could be absorbed onto GF filters. The real distribution system is composed of a huge surface area. Would copper concentration in bulk water keep decreasing if new surfaces were provided continuously, when water is flowing through the system? The following simulation gave an understanding about gradual decrease of copper concentration of a fixed volume bulk water flowing along the pipeline.

1 litre of each sample was filtered by GF filters up to ten times successively. One new GF filter (MN1674, 47mm) was used in every single filtration. Subsequently, 10 identical GF filters were used to filter 1 litre sample of MWR and DW.

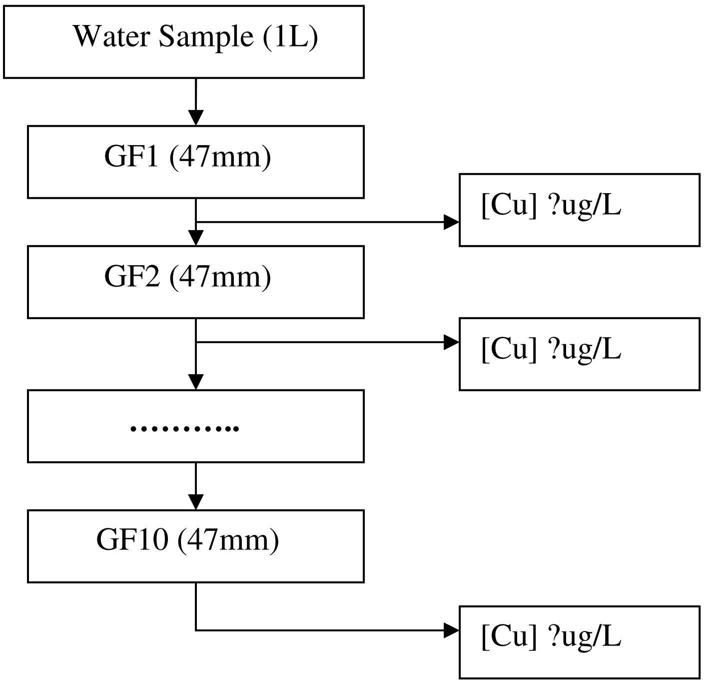


Figure 4.14 The Flowchart of Successive GF Filtration Procedure

Results and discussion

Table 4.8 Results of Successive GF filtration

Filtration Times	MWR [Cu] in filtrate (µg/L)	DW [Cu] in filtrate (µg/L)
0 (Cu dosage)	290	330
1	260	180
2	240	85
3	230	40
4	210	20
5	190	11
6	170	7
7	150	6
8	140	4
9	110	5
10	95	4

Note: ICP method was applied in SGS to measure low copper concentrations.

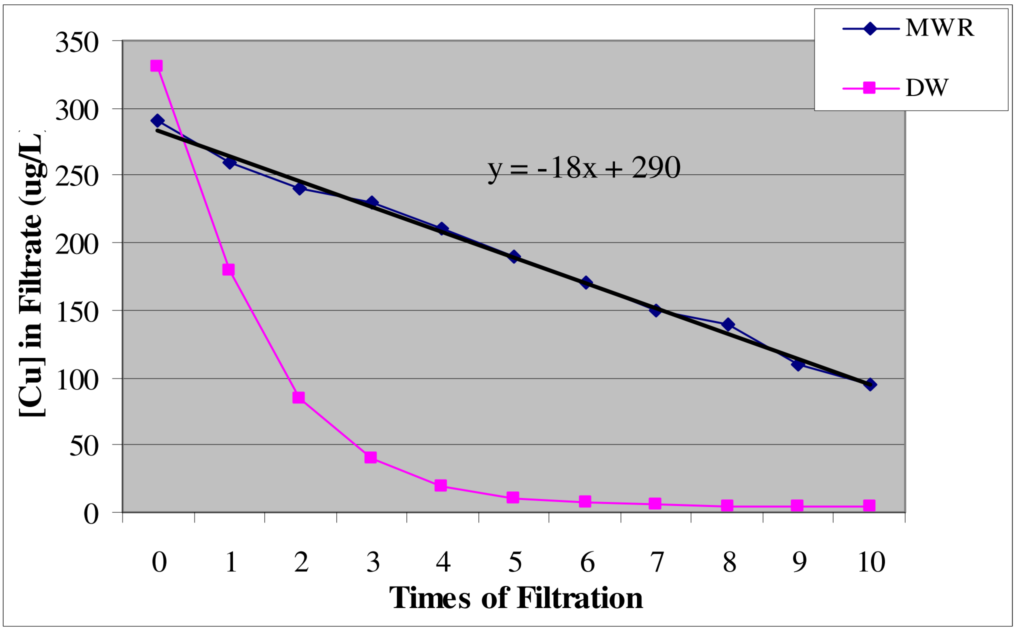


Figure 4.15 Cu Concentrations Vs Times of Filtration during Successive GF Filtration

Discussion

A constant decreasing rate of copper concentrations in Mundaring water sample was shown in Figure 4.15. The decrease appeared linearly proportional to the GF surface area**:** 18μg/piece (47mm GF filter) → 10.4mg/m^2. After passing through 10 pieces of filters (total surface area is around 0.017m^2), 195μg copper in the water was absorbed. Only 95μg/L copper was left in the bulk water. Although it was found that free Cu has the highest affinity to absorb onto the filters, any form of Cu can potentially be absorbed.

Deionised water showed a dramatic decrease of copper concentration. This result also conformed to the performance of DW in the "repeated filtration" experiment. GF filters exert tremendous ability to absorbing Cu^{2+}. Only 4ug/L remaining in the solution indicated almost 330μg cupric ions were absorbed to a 0.017m^2 surface.

Conclusions

Copper contained in bulk water can be continuously taken away via absorption mechanism in the distribution system as long as enough surfaces are provided. Linearly steady decrease of copper concentration showed in Mundaring water (dominated by inorganic and organic copper compounds) while an exponential decrease was observed in deionised water (dominated by cupric ions). The preferred Cu species for absorption is Cu^{2+}.

4.4.3 Continuous GF Filtration

So far GF filters are known to be able to absorb different copper species or compounds. Copper concentrations in Mundaring water successively decreased to a very low level provided enough absorbent area is available. However, the absorptive capacity (μg Cu per unit area) of GF filter to a Mundaring sample is still unknown. In the course of following experiment, a 1400ml Mundaring water sample was filtered continuously through one GF filter (MN1674, 47mm). In order to quantify how the filter can accumulate copper and finally can saturate, copper concentrations were measured in every 200ml filtrate produced continuously in sequence. This experiment was expected to render an understanding of saturation of copper absorption mechanism, because in the real pipeline, a given surface is continuously exposed to flowing water with relatively stable bulk water copper concentration.

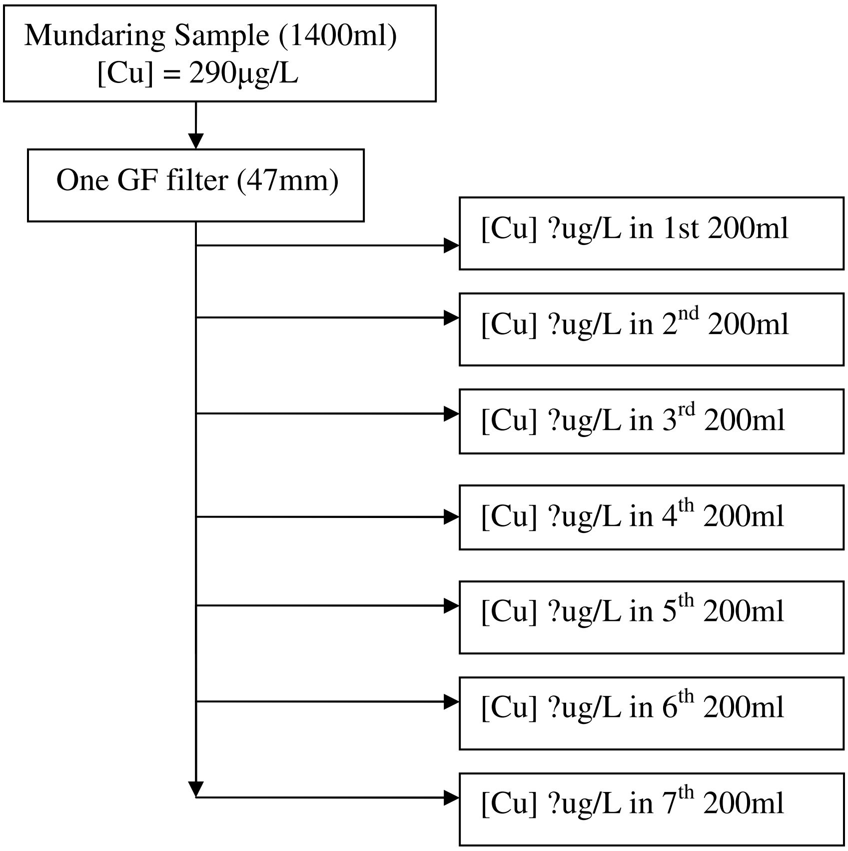


Figure 4.16 The Flowchart of Continuous GF Filtration Procedure

Results and discussion

Table 4.9 Results of GF Continuous Filtration

Unit Volume filtered (ml)	Cu con in the filtrate(µg/l)	Cu absorbed (µg)	Accumulated vol (ml)	Accumulated Cu on filters (µg)
200	220	14	200	14
200	240	10	400	24
200	250	8	600	32
200	260	6	800	38
200	270	4	1000	42
200	280	2	1200	44
200	290	0	1400	44

Note: Copper dosage into Mundaring water was 290µg/L in this experiment.

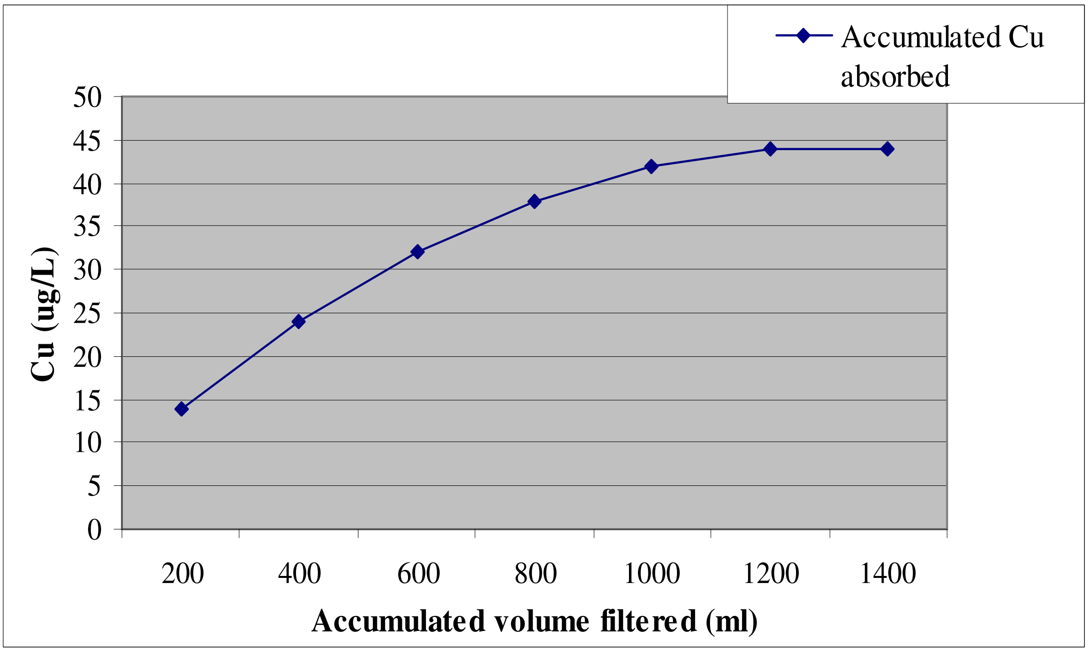


Figure 4.17 Accumulation of Absorbed Copper on One GF Filter during Continuous Filtration of Mundaring Raw Water

Discussion

Figure 4.17 shows an accumulation curve of copper absorbed on one filter. The removed copper was determined as the difference in copper concentration between original and filtered copper times the volume filtered. The volumed filtered in this case is 0.2 L. After a 1400ml sample was filtered by one filter, the copper concentration in the filtrate was 290µg/L, which is equal to the original concentration 290µg/L before filtration. It indicates that the filter is saturated by copper. Consequently, 44µg copper could saturate 1 piece of 47mm GF filter (0.0017m^2). The absorptive capacity of GF filter to absorbing copper compounds in Mundaring water can be expressed as: 26mg/m^2. This capacity was made when bulk water copper concentration is 290µg/L.

4.4.4 Calculation and Summary

A GF filter was used to simulate the absorption mechanism caused by the inner surface of distribution system. The capacity of copper absorbance by GF filter can be calculated:
44μg/piece (47mm GF filter) → 26mg/m^2
Taking a 50km D460 pipeline as an example, to saturate the whole inner surface of pipeline, the amount of copper attached on it would be:

26mg/m^2 x 1445m^2/km x 50km x 10^{-3} = 1875g

However, field copper dosing trials have been under operation for the last 17 months. Taking 10ML/d as an average summer flow rate in C-K extension, copper dosed in the whole distribution system every day is:

0.25mg/L x 10ML x 10^{-3} = 2500g

In terms of the historical data, only 0.1mg/L copper was achieved at the place 50km away from dosing point. So, copper loss in one day is:

0.15mg/L x 10ML x 10^{-3} = 1500g

Consequently, it would take less than two days to saturate a 50km pipe surface according to the calculation, when bulk water copper concentration is maintained at 250μg/L. This comparison indicates that simple surface absorption can not explain the whole mechanism contributing to the loss of copper in the distribution system completely. Nevertheless, real pipe surfaces could have different absorptive capacity considering the situation in the distribution system is much more complicated than GF filters. The absorptive capacity depends on surface roughness, surface material, surface area, layers of calcium carbonate formed on the pipe surface, biofilm…etc. Especially, when aqueous environment in the whole distribution system is in equilibrium with calcium carbonate, layers composed of calcium carbonate can form on the surface of the pipeline, which could provide additional absorptive capacity. Although it is impossible to scrape any samples directly off the surface, sediments accumulated in the pipeline were collected and analysed. The following section focused on specific ingredients found in sediments. The effects on the fate of copper in the distribution system had been investigated.

4.5 The Effects of Ferric Ions and Calcium Carbonate on Organic and Inorganic Bound Copper

So far two conclusions can be drawn from the previous study: naturally gravitational sedimentation account for only a marginal loss of copper from bulk water; simple surface absorption to concrete surface can not explain the loss of copper completely as noticed in the real distribution system. Natural water contains various minerals. There is a good evidence of the presence of high concentrations of Fe, Mn and Ca in sediments along the distribution system. These mineral ions may complex or aggregate with bulk water copper to form compounds or particles, which may attach to or deposit on surfaces of pipelines or sediments. The effects of minerals especially Fe and Ca on the fate of copper were investigated in this chapter.

Sample Preparation and Methodology:

Table 4.10 Description of Water samples in Induced Aggregation

Samples labels	**pH**	**$FeCl_3$ dose(mg/L as Fe^{3+})**	**$CaCO_3$ dose(mg/L)**	**Na_2CO_3 dose (mg/L)**	**UV Abs[1]**	**Alka (mg/L as $CaCO_3$)**
MWRFe-2	8.05	2	0	0	0.45	62
MWRFe-1	8.05	1	0	0	0.45	65
MWRFe-0.5	8.05	0.5	0	0	0.45	65
MWRFe-0.2	8.05	0.2	0	0	0.45	68
MWR-DOCFe-2	8.0	2	0	0	0.18	N/A
DWNaFe-1	8.1	1	0	120	0	55
DWCaFe-1		1	120	0	0	52
DwCaFe-2		2	120	0	0	49

DWNaFe-1: Deionised water + Na_2CO_3 (buffered solution) + Fe (1mg/L) + Copper dosage; pH 8.1 Total Alkalinity 55mg/L as $CaCO_3$. $FeCl_3$ was added into this solution to make the concentration of ferric ions 1mg as Fe/L. A Floc tester was used to mixing $FeCl_3$ and $CuSO_4$ in the water sample, a 200rpm for the initial 2mins (coagulation time). Then, a 20rpm mixing speed was set for the next 30mins (flocculation time). The similar sample preparation process was used for the following samples except the ferric ion concentration was varied (The number followed by the hyphen describes the ferric ion concentration) and Calcium instead of sodium was added: **DWCaFe-2, DWCaFe-1.**

MWRFe-2, MWRFe-1, MWRFe-0.5, and MWRFe-0.2: In Mundaring Raw Water (MWR) samples only ferric chloride and copper were added. Alkalinity or pH in the sample was not adjusted since original pH was around 8.05. Similar to the DW samples, the last number followed by hyphen describes the ferric ion concentration.

Mundaring raw water instead of deionised water was used in these four samples labelled with "MWR". The same ferric chloride and copper dosing were applied to all MWR samples as DWNa samples above.

DWCaFe-2: Deionised water + $CaCO_3$ (buffered solution) + Fe (2mg/L) + Copper dosage; pH 8.0 Total Alkalinity 49mg/L as $CaCO_3$.

DWCaFe-1: Deionised water + $CaCO_3$ (buffered solution) + Fe (1mg/L) + Copper dosage; pH 8.05

MWR-DOCFe-2: Mundaring raw water (DOC reduced) + Fe (2mg/L) + Copper dosage; pH 8.05. MWR-DOC was prepared first (For the procedure of MWR-DOC sample preparation, refer to 3.3.1, Chapter IV). Ferric chloride was added at 20mg/L into Mundaring water. UV absorbance[1] at 254nm (100mm sample cell) was measured before and after coagulation and flocculation.

Abs of MWR = 0.45 per 10cm

Abs of MWR-DOC = 0.18 per 10cm

It indicated that about 60%of DOC had been removed from MWR after coagulation.

Then, $FeCl_3$ (2mg/L) and $CuSO_4$ were added into MWR-DOC. The same mixing and dosing procedure as the above samples were applied.

All the samples had been preserved in an ambient temperature and were kept untouched for 2 days since preparation was completed. Then, copper concentrations in the bulk water and in the filtrate (0.45μm PC membranes were used to separate particulate from filtrate copper) were measured. The same procedure demonstrated in Figure 4.3, was adopted for bulk water copper measurement. To measure bulk water copper concentration, only water 1cm beneath the bulk water surface was drawn.

Table 4.11 Results of Fe Dosage VS Cu-containing Particulate Formation in Mundaring water

Sample label	**MWRFe-2**	**MWRFe-1**	**MWRFe-0.5**	**MWRFe-0.2**
[Fe] dosage (mg/L)	2	1	0.5	0.2
[Cu] dosage (ug/L)	250	250	250	250
Bulk $[Cu_T]$ test (μg/L)[1]	190	210	220	230
[Cu] in filtrate (μg/L)[1]	10	50	140	190
Cu blocked by filters (μg)	240	200	110	60

Note: "Bulk [Cu]" means Cu concentration in the testing water sample drawn from 1cm beneath the surface of the bulk water (refer to Figure 4.3).

[1] Copper measurement has an error of ±10μg/L and a lower detection level of 20μg/L.

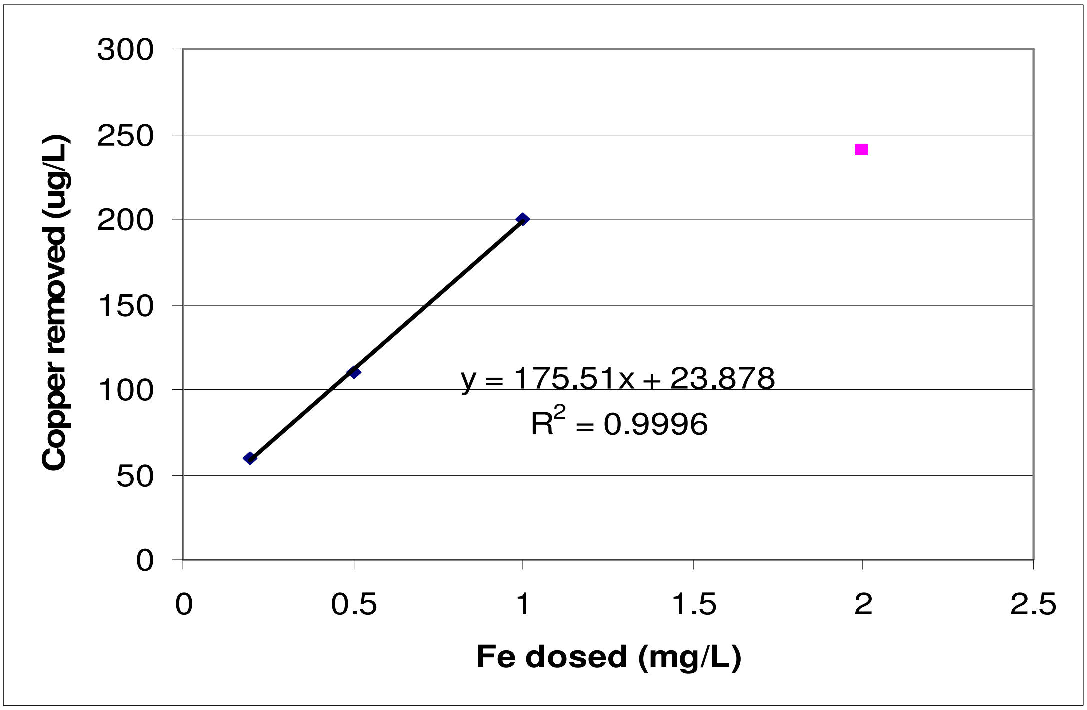


Figure 4.18 Copper Removed as a Function of Fe Dosed (The last point (Fe concentration of 2 mg/L) is not considered since copper is removed in the sample to below detection limit. Copper removal is at 176μg-Cu per every mg of Fe dosed)

Table 4.12 Results of Ferric ion Induced Cu-containing Particulate Formation in Carbonate Buffered Water

Sample label	DWNaFe-1	DWCaFe-1	DWCaFe-2	MWR-DOCFe-2
[Fe] dosage (mg/L)	1	1	2	2
[Cu] dosage (µg/L)	250	250	250	250
Bulk [Cu] test (ug/L)[1]	160	80	30	60
[Cu] in filtrate (µg/L)[1]	110	60	30	50
Cu blocked by filters (µg)	140	190	220	200

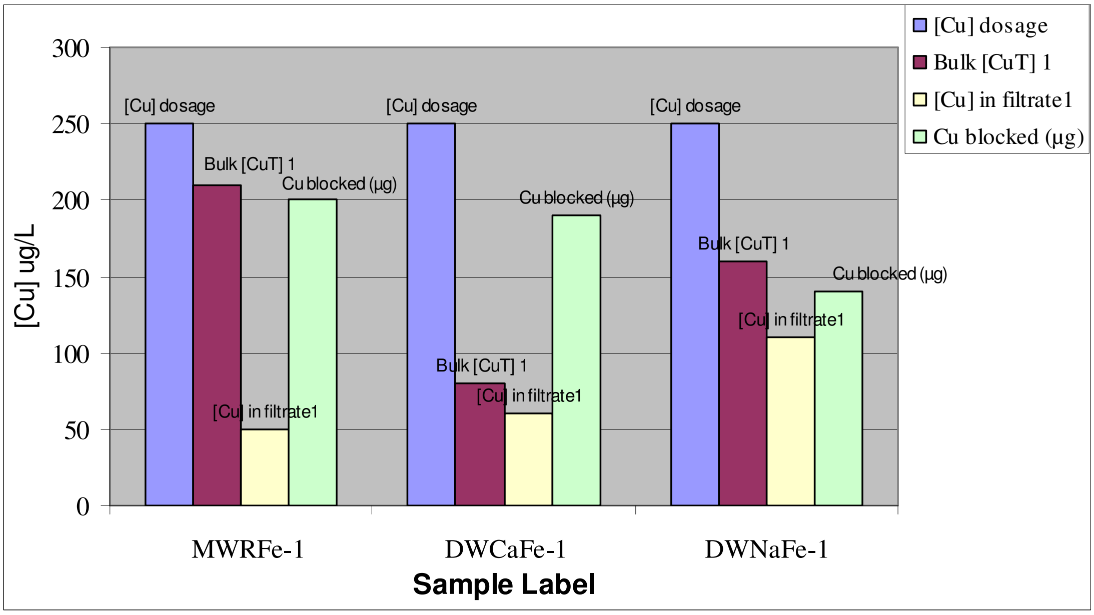


Figure 4.19 Comparison of Fate of Copper among Mundaring Water (MWR), Na_2CO_3 and $CaCO_3$ Buffered Deionised Water (Fe dose was 1mg-Fe^{3+} /L)

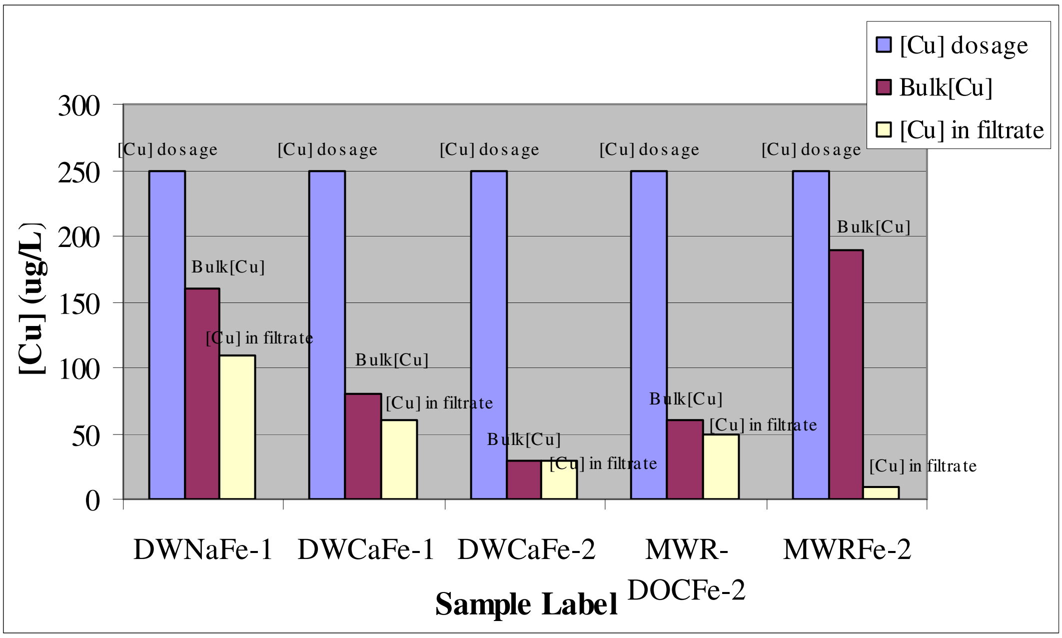


Figure 4.20 Comparison of Cu-containing Particulate Formation in Buffered Solutions and Mundaring Water

Discussion

In the MWR samples, the addition of ferric ions has removed copper from the solution. The copper removal seems to be proportional to added Fe (Figure 4.18). About 176µg copper per mg of ferric ions was removed from solution. Probably, ferric ions in the bulk water are capable of forming relatively large size Cu-containing particles (>0.45µm). At pH 8, ferric ions exist mostly as $Fe(OH)_3$ (Vernon L. Snoeyink, 1980). The Cu-containing substances, irrespective of particles or dissolved forms, could attach to ferric hydroxide. In the case of 2mg-Fe/L, almost all the copper is removed leaving just 10µg/L. This value is below detection level. Therefore, this value is omitted in calculating 176 µg Cu per mg of ferric ions.

Figure 4.19 demonstrated that although copper appears to be in solution in Mundaring raw water, when filtered both calcium carbonate buffered water and Mundaring raw water showed similar behaviour. These results indicated that copper exists as particulates in the presence of ferric ions irrespective of whether copper exists as organically or inorganic bound. In addition, compared to sodium carbonate containing water, calcium carbonate can assist copper sedimentation and particulate formation

(Figure 4.19 and Table 4.11). This is demonstrated when DWNaFe-1 showed 160ug/L and 110ug/L of copper in bulk water and filtrate respectively, while only 80ug/L and 60ug/L of copper in corresponding circumstances were observed in calcium carbonate buffered solution (DWCaFe-1).

Most copper was agglomerated into large particles and removed by 0.45μm membrane filtration when Fe^{3+} was present in Mundaring water, DOC-removed Mundaring water and calcium carbonate buffered solution (shown in Figure 4.20). Relatively higher "bulk [Cu]" found in Mundaring water was probably due to the lower density of organic-Cu aggregates suspended in bulk water instead of inorganically bound copper in calcium carbonate buffered water. In DWCa water samples, copper solubility is controlled by a calcium carbonate buffered system. The main forms of copper include CuO (tenorite) and inorganic copper compounds ($CuCO_3^o$, $CuOH^-$) ((Vernon L. Snoeyink, 1980). DOC-removed Mundaring water has a similar behaviour as that of DWCa samples. Comparing "bulk [Cu]" in MWRFe-2 and MWR-DOCFe-2, 130μg/L more was found in MWRFe-2 sample. This could be contributed partly by organic matters existing in Mundaring raw water (70~80ug/L organic-Cu compounds in MWR, Figure 4.11). Similar filtering results were achieved in these three kinds of samples. Consequently, the majority of copper compounds had been agglomerated into large particles no matter what their forms.

Conclusion

When ferric ions are present in bulk water, copper with various species, including organic and inorganic copper compounds can be coagulated and aggregated into large particles able to be filtered by a 0.45um membrane. Even 0.2mg/L ferric ions can get rid of 60μg/L copper from bulk water. This highlights the substantial sink of the copper. Filterable copper formed in aggregation appears linearly proportional to concentrations of ferric ions. 1mg/L ferric ions can remove 200μg/L of copper. Furthermore, calcium carbonate can assist Cu-containing particles, sedimentation and aggregation.

CHAPTER 5

FIELD DATA ANALYSIS AND DISCUSSION

5.1 Introduction

A pilot copper dosing trial has been undertaken in the C-K extension system for the last 18 months (04/2006 to 09/2007), it is still continuing. Along one section (about 58km) of main pipeline from the copper dosing point (Cunderdin) to the service water tank (Minivale), filed data were collected and steady copper decrease along the pipeline was observed. Copper concentrations have been measured periodically at three points: Cunderdin dosing point, 12.1km (C-K12.1km) and 58km away (C-K58km, inlet of Minnivale tank) from Cunderdin dosing point respectively. Sediments in the pipeline have been drawn and analysed at two points: 11km (C-K11km) and 50km (C-K50km) away from Cunderdin dosing point respectively. Sediments were collected by flushing the target pipe sections using hydrants.

5.2 Analysis of Sediments Data and Discussion

Cu-containing sediments in the pipe could either be produced by gravitational sedimentation of large particles or deposition of aggregates onto the inner pipe surface or sediments. This section compared the lab results achieved from Chapter 4.5 with the field sediments data in order to reveal whether induced aggregation by mineral ions is one mechanism leading to loss of copper in the field.

Altogether the experimental results predicted that in the presence of Fe^{3+} almost all forms of copper can be removed at the ratio of 176 μg-Cu/mg-Fe^{3+}. That means at saturation, copper-ferric ratio in sediments will be approximately 18%. In sediments where saturation has already taken place this ratio should be satisfied. If the ratio is less than this, the sediment is not saturated. On the other hand, other processes could remove copper from bulk water in the distribution system. For instance, calcium carbonate was found to be capable of aggregating more copper and hence would introduce more sediment (Figure 4.20). Therefore, higher copper percentage than reported in the calculation is possible.

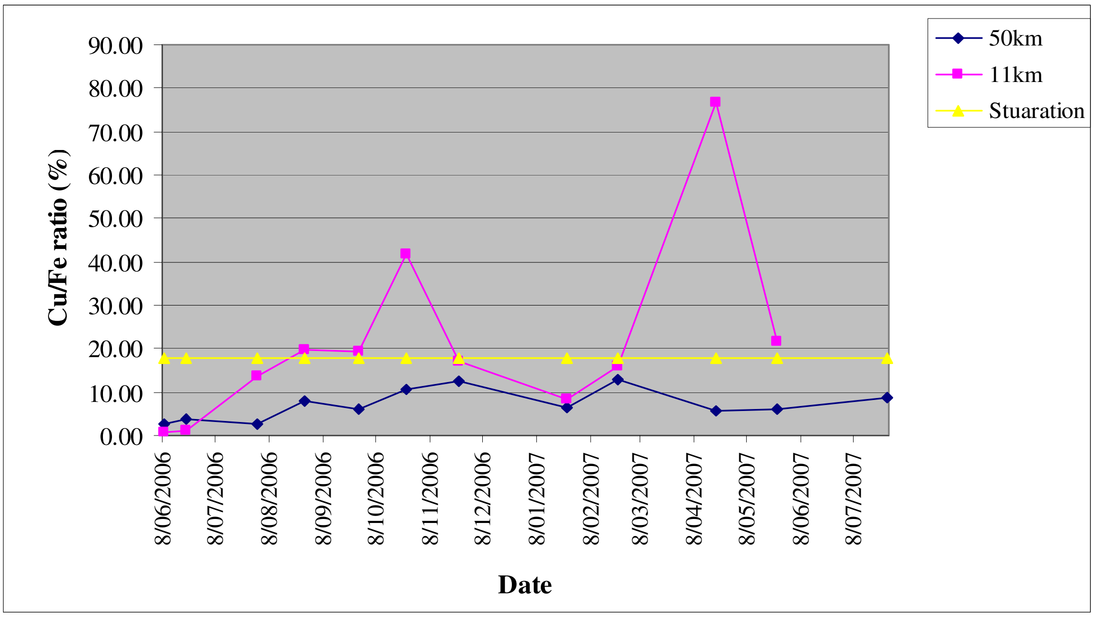


Figure 5.1 Cu/Fe Ratios in Sediments Collected from 50km and 11km along C-K Extension (raw data was provided by Laszlo Koska, Water Corporation, WA)

(The triangle line represents saturation line (18%), deduced from the calculation of Figure 4.18)

In Figure 5.1, all data collected from 50km lie below the saturation line. This indicates that sediments in 50km spot have not been saturated so far and copper will be continuously lost in this area until the calculated Cu/Fe ratio is satisfied. However, some high Cu/Fe ratios (41% and 76%) were found in sediments from C-K11 place. This indicated that there is some other mechanism that can accumulate more copper in the sediment.

If the sediment is already saturated in the initial part of Cunderdin, what happens to the copper that is disappearing from bulk water? There are three plausible explanations for this:

1. Inlet water to Cunderdin copper dosing pumps release enough ferric ions to remove dosed copper.
2. There are local pockets of corroding iron pipe that continuously leak ferric ions.
3. There are some other mechanisms or factors which contribute to the copper loss.

Table 5.1 Composition of Cu, Fe and Ca in Sediments along C-K Extension (data was provided by Paul Nolan, Water Corporation, WA)

C-K 50km					C-K 11km				
Date	**Fe(mg/kg)**	**Cu(mg/kg)**	**Ca(mg/kg)**	**Cu/Fe ratio(%)**	**Date**	**Fe(mg/kg)**	**Cu(mg/kg)**	**Ca(mg/kg)**	**Cu/Fe ratio(%)**
8/06/2006	45630	1168	132043	2.56	8/06/2006	39283	338	3571	0.86
21/06/2006	127167	4818	6061	3.79	21/06/2006	77405	958	7742	1.24
1/08/2006	219747	5914	6593	2.69	1/08/2006	57057	7696	7143	13.49
28/08/2006	72359	5848	4655	8.08	28/08/2006	32405	6378	5405	19.68
28/09/2006	174975	10404	8750	5.95	28/09/2006	99575	19225	10000	19.31
25/10/2006	85686	9261	11429	10.81	25/10/2006	33208	13917	33333	41.91
24/11/2006	86251	10969	5490	12.72	24/11/2006	87466	14972	2500	17.12
25/01/2007	57741	3690	5926	6.39	23/02/2007	118625	9894	6250	8.34
23/02/2007	118188	15375	18750	13.01	20/04/2007	126455	20091	18182	15.89
20/04/2007	249896	14302	8333	5.72	25/05/2007	32228	24735	7353	76.75
25/05/2007	214727	12955	3030	6.03	27/07/2007	34392	7468	2400	21.71
27/07/2007	157686	13817	4615	8.76					
Average	**134171**	**9043**	**8056**	6.74		**67100**	**11424**	9444	17.03

Note:

Along the main pipeline from the copper dosing point (Cunderdin) to the service water tank (Minnivale), sediments have been drawn and analysed at two places. One is 11km away from Cunderdin (C-K11km), the other is 50km away from it (C-K50km). Sediments were collected by flushing the target pipe sections using hydrants.

The first point could easily be tested by measuring bulk water coming into the Cunderdin copper dosing pump.

The second point could be tested in many different ways. For example, robot-camera patrolling in the pipeline could be used to check any cracks on inner surface. Iron corrosion is possible because of historically wide temperature variation the pipes were exposed to, and the material pipes were made. An outer steel pipe can expand/shrink more than an inner cement lining. Cement can withstand the shrinking of steel but not the expansion of steel at higher temperatures. Hence, it is very much possible that there are cracks in the above ground pipe line rather than in the underground pipeline. This can only be checked by physically inspecting the pipeline. If any cracks occurred in the pipeline, the corroding metal surface would expose in the bulk water.

Vernon L. Snoeyink and David Jenkins reported that natural water could be saturated, at equilibrium, or oversaturated with $CaCO_{3(s)}$. Langelier Index (L.I) helps in understanding the status of the water. When L.I is zero, water is in equilibrium with $CaCO_{3(s)}$. If L.I is positive, the water is oversaturated with $CaCO_{3(s)}$ and tends to precipitate more $CaCO_{3(s)}$; if L.I is negative, the water is under saturated and tends to dissolve $CaCO_{3(s)}$.

L.I = pHa – pHs
pHa: actual pH of water

pHs: pH of water if it were in equilibrium with $CaCO_{3(s)}$ at the existing solution concentration of HCO_3^- and Ca^{2+}.

Mostly, bulk water in the pipeline could be regarded as a closed system to the atmosphere, in which alkalinity and pH might be relatively high ($pH_a > pH_s$). When water is oversaturated and keeps precipitating $CaCO_{3(s)}$, these precipitates can form a cover on the surface of pipeline which could absorb copper in bulk water. If water is historically oversaturated with $CaCO_{3(s)}$, then it is possible that the surface is well coated by $CaCO_3$(s) layers.

However, nitrification was reported historically happening in this part of the distribution system. Nitrifiers carried in the pipeline can decrease pH and probably lead to negative L.I. In this case, $CaCO_{3(s)}$ would keep dissolving so the inner surface could not be protected. This can expose the concrete surface or any other surface to bulk water contents. Consequently, the corroding metal surface would find the chance to release ferric and coagulate all copper species in bulk water. According to the calculations in the experiments, for the continuous loss up to 200μg/L of copper, only 1mg/L ferric ions are needed. Given all these conditions, it is possible to lose copper at the rate observed in the distribution system.

In addition, chlorine and chloride in the bulk water can act as oxidants which can oxidize Fe to Fe^{2+} and Fe^{3+}. Ferric ions could be continuously produced and agglomerated with copper compounds and all copper species. Although Cu^{2+} hardly exists in Mundaring water at pH 8, the possibility can not be excluded that Cu^{2+} may exist in the distribution system at trace levels. Especially, when nitrifiers carried in the distribution system lead to the low pH, Cu^{2+} could be released. Galvanic cells would be formed in the pipeline which could result in the Copper/Fe ratio much higher. To understand this physical observation, the existence of elemental copper should be understood.

	ΔG^o (kcal)	$-nFE^o$
$Cu^{2+} + 2e = Cu(s)$	-15.68	-2F (+0.34)
$Fe(s) - 2e = Fe^{2+}$	-20.29	-2F (+0.44)
$Cu^{2+} + Fe(s) = Cu(s) + Fe^{2+}$	-35.97	

Theoretically, in a standard condition, this redox reaction will automatically take place forwardly. The accurate free energy data could be calculated provided ferric ions, temperature were known. Furthermore, chlorine in the bulk water is a strong oxidant which can convert Fe and ferrous ions to ferric ions. To sum up, the vicinity of certain areas of corroding iron pipe can be an unlimited ferric ions source responsible for continuous or suddenly dramatic copper loss in some specific places.

In order to understand and quantify how ferric and calcium ions can aggregate copper species, the concentrations of these ions in bulk water should be analysed. Although the direct data in C-K extension pipes are not available, some bulk water data around this vicinity revealed that the concentration of ferric ions is around 0.03~0.08mg/L, calcium ions 18~25mg/L and manganese 0.002~0.004mg/L. The concentrations of ferric ions in bulk water indicate much lower than as applied in the laboratory experiments. However, the possibility of high concentrations in some places where pipes corrode can not be excluded. The maximum Fe^{3+} ion concentration that could be measured is 0.188 mg/L at pH8. Calcium ions can also be considerably increased by pHs drop somewhere nitrification takes place.

The third point mentioned other unknown factors which could impact the fate of copper. However, a complete analysis of composition of bulk water in distribution system has not been done so far as a comprehensive investigation could not be undertaken. For example, in previous experiments, calcium carbonate was found able to assist Cu-containing particles aggregation. The contribution from calcium carbonate existing in distribution system is stilled not quantified. At the moment when nitrification is under control due to inhibitor dosing, the water could be expected to be slightly oversaturated. The distribution system is probably in equilibrium with calcium carbonate buffered system. Calcium carbonate sediments or coating on the surface could augment copper sedimentation and deposition. Consequently, more copper loss than what had been calculated simply from Fe/Cu ratio (Figure 4.18) is possible.

5.3 Analysis of Field Bulk Water Data and Discussion

From April 2006 to August 2007, copper concentrations in bulk water along part of C-K main pipeline were measured periodically. Three places were chosen as target points: Cunderdin dosing point, C-K12.1km and C-K58km (inlet to Minnivale tank). Complying with the approval by Department of Public Health, copper dosage in this pilot field experiment ranged from 0.25mg/L to 0.4mg/L.

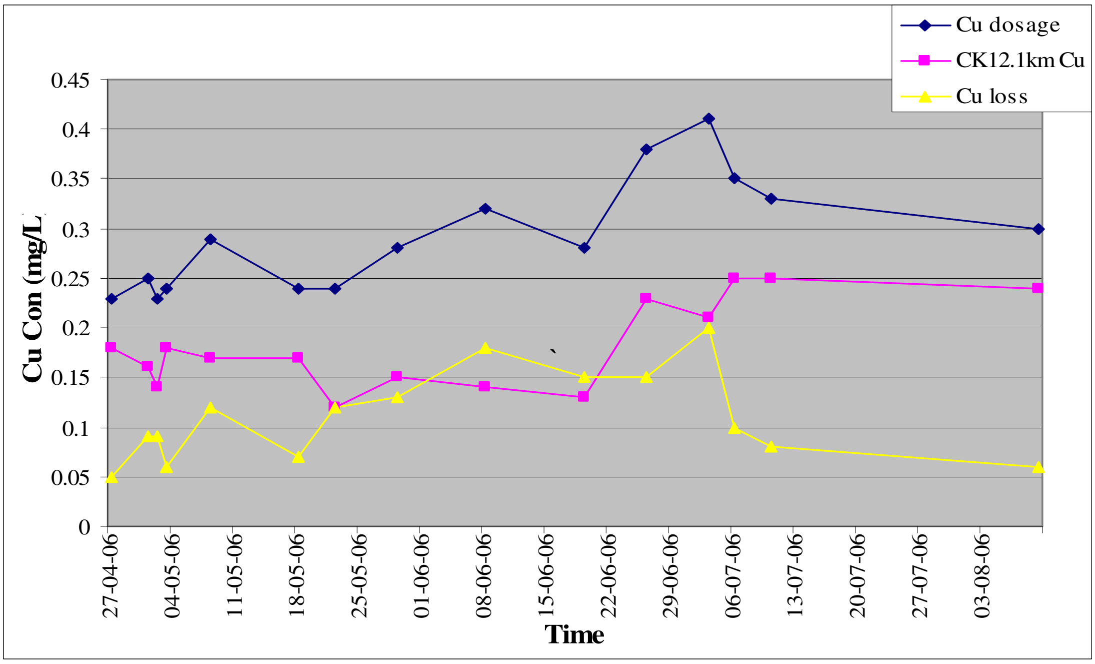


Figure 5.2 Historical Data of Copper Dosage and Concentration (April to August 2006) of C-K12.1km along C-K Extension (raw data was provided by Laszlo, Koska, Water Corporation, WA)

("Cu loss" was simply calculated by deducting dissolved copper concentration from "Cu dosage")

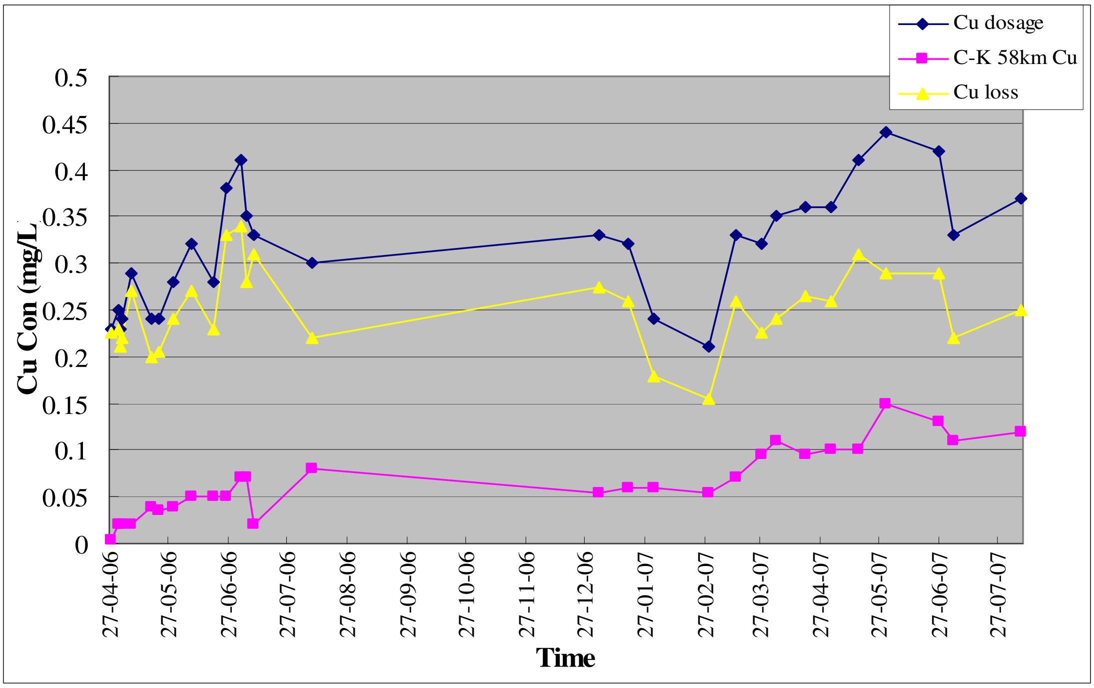


Figure 5.3 Historical data of Copper Dosage and Concentration (April 2006 to August 2007) of C-K58km along C-K Extension (raw data was provided by Laszlo Koska, Water Corporation, WA)

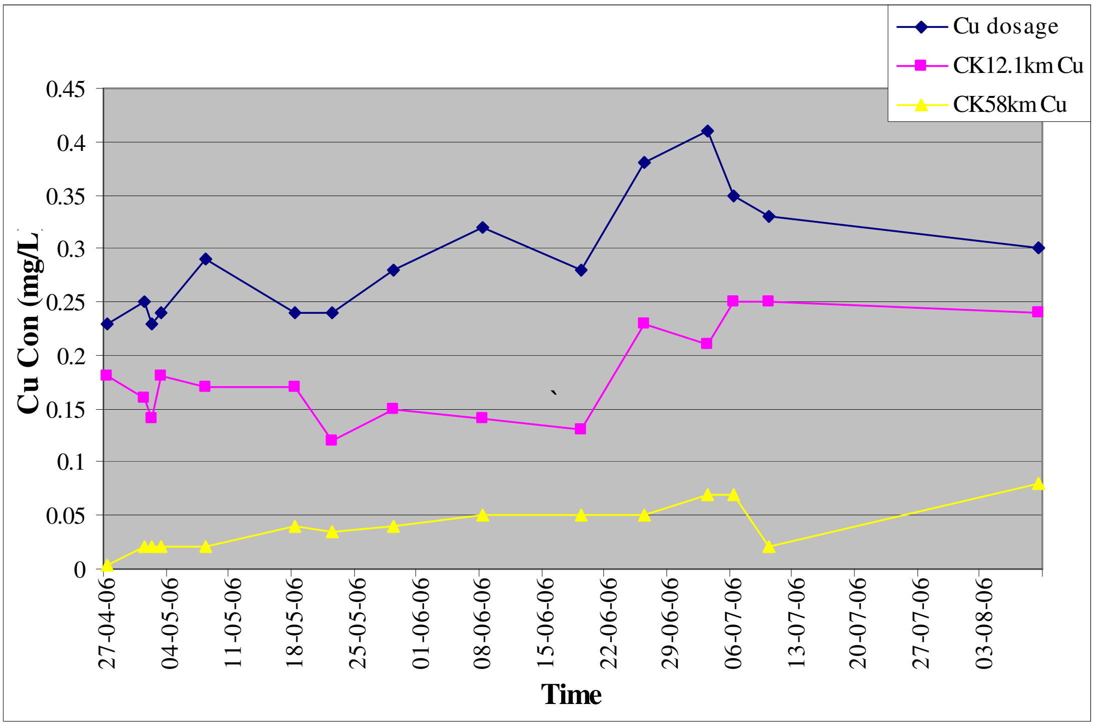


Figure 5.4 A Comparison of Historical Data of C-K12.1km and C-K58km (April to August 2006) (raw data was provided by Laszlo Koska, Water Corporation, WA)

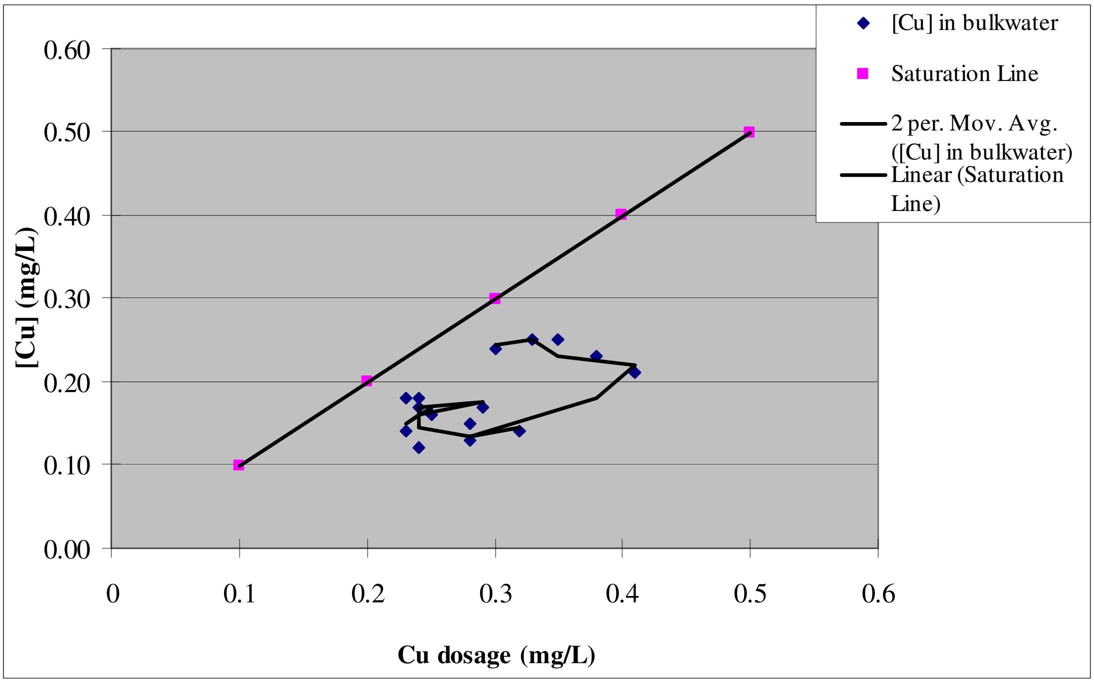


Figure 5.5 Theoretical Saturation Line Vs Copper Concentration in C-K12.1km Based on Historical Cu Dosage

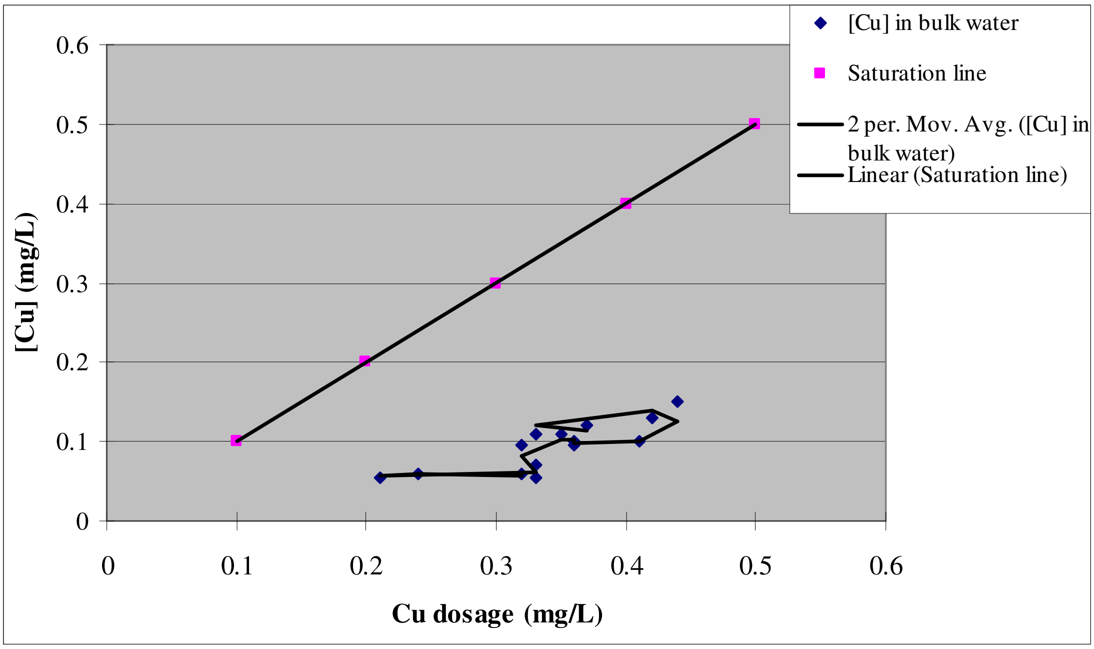


Figure 5.6 Theoretical Saturation Line Vs Copper Concentration in C-K58km Based on Historical Cu Dosage

Discussion

In two different places (C-K12.1km and C-K58km), zigzag lines of copper loss demonstrated a similar trend to copper dosage lines (Figure 5.3 and Figure 5.4). It indicated that both copper loss and bulk copper concentrations are positively related to copper dosage. In addition, during the trial experiments, bulk copper concentrations in these two places showed a generally increasing trend in spite of some fluctuation. This result seems linked to the saturation phenomenon. If the pipeline could be saturated by copper, that would take place in sequence along the distance of the pipe. Figure V 2.4 further compares historical copper concentrations in both C-K12.1km and C-K58km. On average, copper concentrations in C-K12.1km showed around 0.14mg/L higher than those in C-K58km. Subsequently, adsorption is reasonably speculated to be one possible mechanism leading to loss of copper in the distribution system.

Nonetheless, after 17 months trial, the adsorption equilibrium has not been reached. Figure 5.5 and Figure 5.6 showed the theoretical saturation lines and the historical data of bulk copper concentration. Under a constant concentration of copper dosage, if the pipe were saturated, the bulk copper concentration should be equal to the copper dosage.

In other words, no copper loss would happen in the pipeline. The vicinity of "[Cu] in bulk water" is completely beneath the saturation line in Figure 5.5. It indicates that C-K12.1km pipe is not saturated but it is very close to it compared to C-K 58km. Figure 5.6 shows that C-K 58km pipe is much further from saturation. Especially when copper concentration increased to 400µg/L and then when it is reduced to 300 µg/L saturation seemed to be achieved.

In fact, the real pipe could have a tremendous adsorptive capacity because: Composites of real pipe surfaces are much more complicated than GF filters. Except ashes on it, biofilm could play a role of absorbing copper; surfaces coated by $CaCO_3$ would not be easy to saturate because calcium ions continuously brought into the pipeline could build up new surfaces endlessly.

However, the adsorption mechanism alone can not explain the copper loss completely, for other factors also contribute to the fate of copper, for instance, ferric ions and calcium carbonate found in sediments. Their effects have been proved in previous experiments. In order to separate the two mechanisms controlling the fate of copper, laboratory models need to be built up to quantify both of them. Effects from ferric ions had been quantified in the laboratory so far. To quantify adsorption mechanism, field data is not reliable because copper dosage was fluctuating so that no constant copper concentration could be maintained for a long time. To build up Langmuir isotherm and BET isotherm, samples with various copper concentrations can be prepared. Each sample with constant concentration could be filtered by GF filters or flow through a section of pipe continuously. Then, the adsorptive capacity of surface could then be found. Relationship between C/y and C could be plotted.

Langmuir isotherm equation: $C/y = a/y_m + C/y_m$
BET isotherm equation: $y/ym = bC/(Cs-C)[1 + (b-1)C/Cs]$
y_m: maximum capacity of adsorption
C: concentration of adsorbate
Cs: saturation concentration for adsorbate
a and b: constants

Using this relationship, a better understanding of adsorption in the real system could be reached. This would lead to deduction of loss of copper contributed by adsorption. Subsequently, these two potential mechanisms can be separated and quantified. This thesis does not include comprehensive laboratory modelling of these adsorption mechanisms and further work need therefore to focus on quantifying this mechanism and separating two of them.

Chapter 6

SUMMARY, DISCUSSION AND RECOMMENDATIONS

6.1 Summary and Discussion

6.1.1 Major Forms of Cu-containing Compounds in Bulk Water

As a strategy of protecting chloramine against nitrification in a drinking water distribution system, cupric sulphate has been dosed directly into the pipeline to control nitrifying bacteria. However, almost no free cupric ion regarded as the most toxic and effective form to inhibit bacteria can exist in bulk water although in trace levels. On the other hand, copper hydroxide ($Cu(OH)_2$) is not the main Cu-containing form. Instead, most of the dosed copper initially reacts or combines with chemicals or aquatic substances in bulk water and turns into the following main forms:

- Organic copper compounds: water bodies in dams or pipeline contain various dissolved organic matters which combined with copper and formed dissolved organic copper compounds.

- Inorganic copper compounds: natural water in distribution system is usually buffered by calcium carbonate system, where copper combines with CO_3^{2-}, OH^-, HCO_3^- and forms inorganic copper compounds such as $CuCO_3^o$, $Cu(OH)_x^{2-x}$…etc. In addition, tenorite (CuO) could form in a carbonate buffered system in natural water and exist as fine particles.

6.1.2 The Fate of Copper in the Distribution System

The fate of copper research was initialised from three basic mechanisms: sedimentation, adsorption/biofilm, induced particle aggregation and deposition. Samples containing different copper species were involved in experiments investigating each mechanism.

Gravitational sedimentation could not happen in bulk waters, no matter what forms of copper are (organic or inorganic copper compounds). Furthermore, organic and inorganic copper compounds exist in bulk waters as dissolved forms instead of particulates. So, Cu-containing particles would not naturally form in bulk waters.

Adsorption is considered one potential mechanism taking copper away from bulk waters. This mechanism was simulated in glass fibre filtration experiments. GF filters are capable of absorbing various copper species, including soluble copper. Among these copper species in bulk water, organic copper compounds appeared relatively stable against adsorption. However, copper concentrations could continuously decrease to zero as long as enough surface areas were provided. Surfaces could be saturated and the absorptive capacity of a GF filter was quantified when copper concentration was maintained at 290µg/L. However, GF adsorption can not explain the loss of copper in the field completely. Possible reasons for this difference have been given. One concerns the tremendous adsorptive ability of the real pipes. The inner surface composites of real pipelines are much more complicated than GF filters. Biofilm is inaccessible and not analysed. Calcium carbonate could coat on surfaces and assist adsorption. On the other hand, if the pipe were continuously exposed to nitrifying water, L.I could be negative and calcium carbonate would dissolve. In this case, corroding pipes could find some places to leak ferrous ions into bulk water which could result in mineral ions induced aggregation.

Mineral-causing (Fe^{3+} and Ca^{2+}) particulate aggregation and subsequent deposition was demonstrated in the laboratory as one of the mechanisms leading to dramatic copper loss in the distribution system. Ferric ions in bulk water can form ferric hydroxide which causes Cu-containing substances aggregating to large particles. Subsequently these aggregates could be deposited on rough surfaces of pipelines or sediments. In addition, calcium carbonate dominating in carbonate buffered system in bulk waters could help sedimentation of Cu-containing aggregates. Ferric ions demonstrated a strong ability to aggregate Cu-containing compounds. Sediments analysis in the field study showed a large amount of Fe and Cu contained in pipeline sediments. Most sediments data collected showed a good match with laboratory results. The Cu/Fe ratio (18%) which is calculated in the laboratory experiments almost agreed with what was observed in the field data. All that is needed to aggregate with 175µg-Cu/L is just 1mg-

Fe/L. However, some field data did not fall in line with lab experiments. This indicates other plausible mechanisms leading to a dramatic loss of copper. For instance, $CaCO_3$ balanced by buffered system could be coated on the inner surface of pipeline and reinforce deposition. In addition, considering Goldfield distribution system's long history (100 years) and wide temperature fluctuation, cement pipe cracks and ferric ions leakage from corroding iron pipes are possible. The negative L.I caused by nitrification can also help dissolve calcium carbonate and release ferric ions from leaking pipe surfaces. Redox and galvanic cells reactions between Cu and Fe can take place. As long as plenty of ferric ions are provided, dramatic copper loss much more than was observed in the laboratory could happen.

6.2 Recommendations for Further Research and for Water Utilities

6.2.1 Recommendations for Further Research

Through this research, fundamental copper forms dominating in bulk water have been identified and factors controlling these were found and quantified. Possible mechanisms leading to copper loss were investigated one by one. One mechanism controlling the fate of copper was identified and quantified. The other potential mechanisms are suggested. However, to thoroughly understand the fate of copper in the distribution system and inhibition effectiveness, the following further studies are recommended:

- Comprehensive bulk water analysis from a distribution system needs to be done to find out concentrations of some specific mineral ions (Fe^{3+}, Ca^{2+}) in inlet and outlet of target pipeline. Inspect any pipe cracking places to analyse the intensively concentrated mineral situation. It will help complete quantifying impacts on the formation of Cu-containing particles from the effects of mineral ions.
- Further laboratory experiments need to be undertaken to quantify the effects contributed by adsorption in the distribution system. A real section of the pipeline could be taken as a model to simulate the surface adsorption mechanism.

● Instead of dosing cupric sulphate, some laboratory analysis concerning chelate copper complexes (cupricide-algicide and coptrol) should be undertaken. Fate of these copper complexes would be investigated.

● The effectiveness of different copper compounds and species need to be investigated to find out which form(s) can be effective in inhibiting nitrification.

6.2.2 Recommendations for an Inhibition Strategy in Water Utilities

The results reported in the thesis suggest that there are many sinks for copper in the distribution system. Even organic copper compounds, which demonstrated comparatively better stability, could be taken away by ferric ions aggregation and adsorption onto the wall or sediments. Variables in a long pipeline are very difficult to control. However, water reservoirs are relatively stable systems. According to bulk water experiments, copper compounds would remain stable without continuously introduced mineral ions and in contact with huge surface areas such as a long pipeline surface. In addition, reservoirs are regarded as places which could collect detached biofilm and might grow nitrifying bacteria. Consequently, it would be worth considering dosing copper into reservoirs to inhibit nitrification growth and assist disinfection, instead of dosing copper directly into pipelines. In this case, nitrifying bacteria could be controlled within defined boundaries rather than extended into the whole distribution system. In order to implement this strategy effectively, instead of dosing copper at one point, multi-dosing points are needed in different reservoirs along the long distribution system. By controlling the growth or accumulation of nitrifying bacteria effectively in reservoirs, nitrifiers released into the pipeline from reservoirs could be minimized.

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Appendix A

Results of Total Chloramine Decay

Chemical Decay Vs Microbiologically Assisted Decay

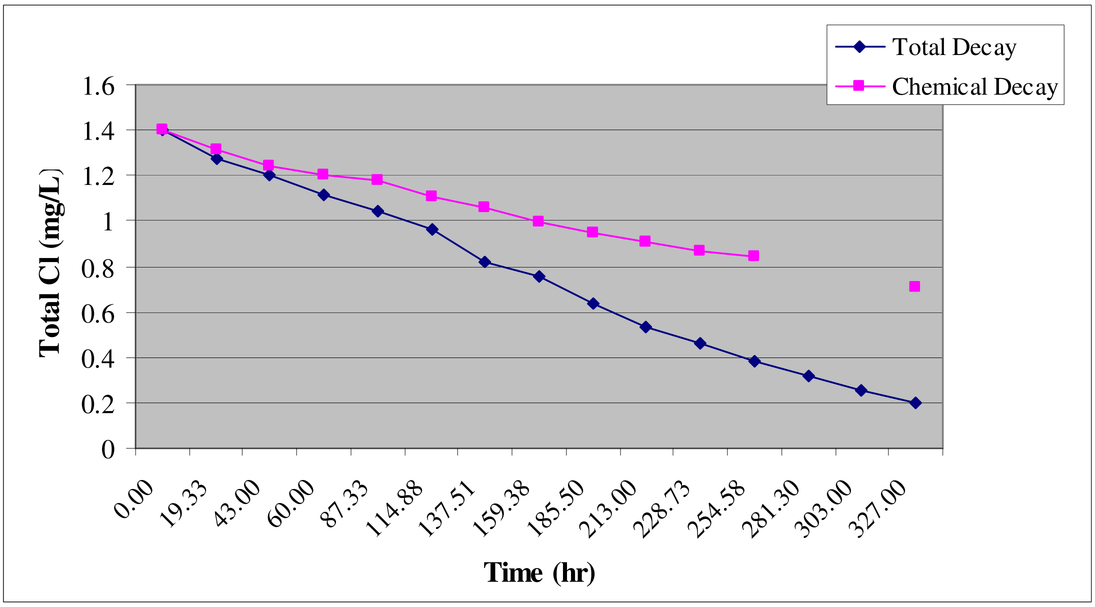

Figure A1 Comparison between Inhibited and Unprocessed Sample (sample 1)

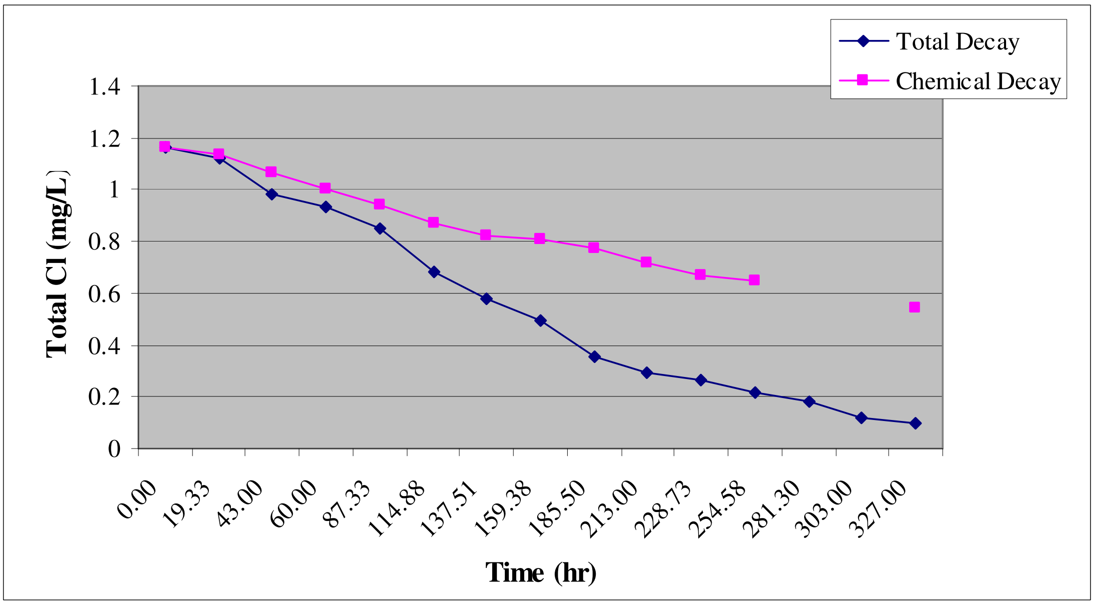

Figure A2 Comparison between Inhibited and Unprocessed Sample (sample 2)

Note: Sample 1 and Sample 2 were collected from two places within C-K reticulation system, where nitrification was detected. Silver nitrate was used as an inhibitor.

Sample 1: Kc = 0.0021 hr^{-1} Km = 0.0039 hr^{-1} Fm = 1.86 (Fm = Km/Kc)

Sample 2: Kc = 0.0032 hr^{-1} Km = 0.0045 hr^{-1} Fm = 1.41 (Fm = Km/Kc)

Appendix B

Results of Copper Hydroxide ($Cu(OH)_2$) Filtration Using 0.2µm and 0.45µm Membranes

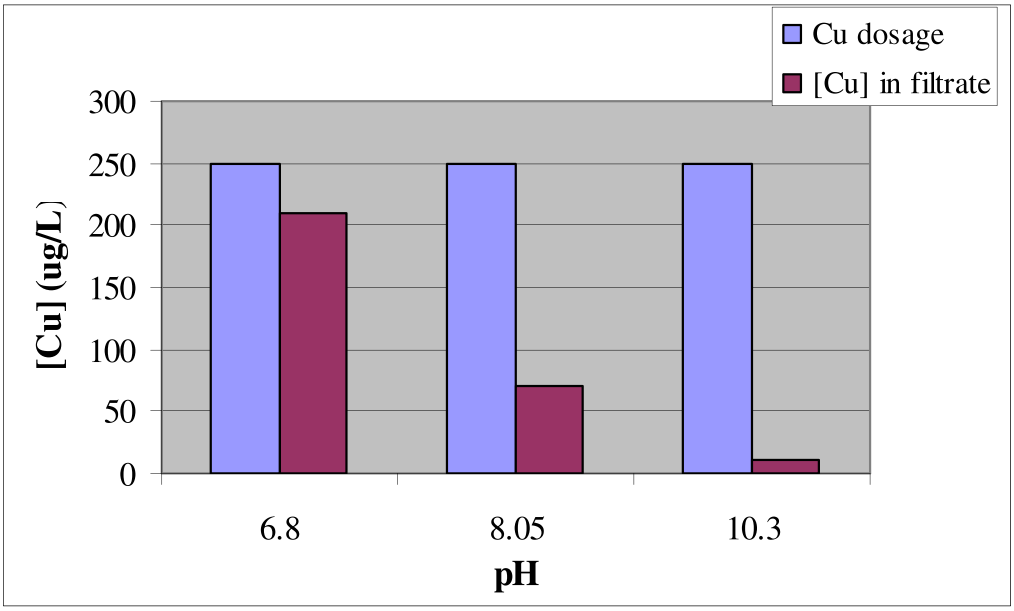

Figure B1 0.45µm CA (Cellulose Acetate) Membrane Filtration

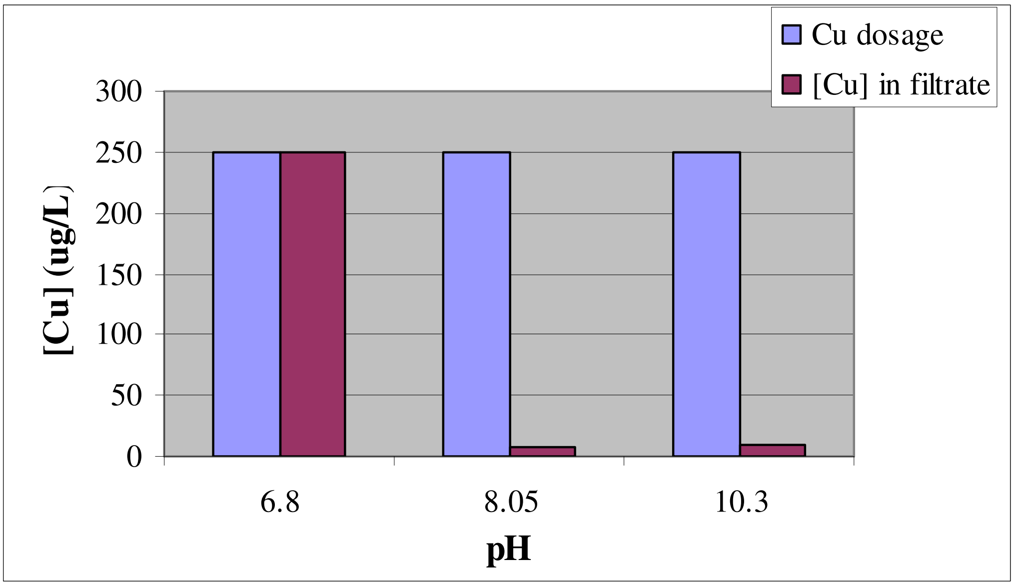

Figure B2 0.2µm CE (Cellulose Ester) Membrane Filtration

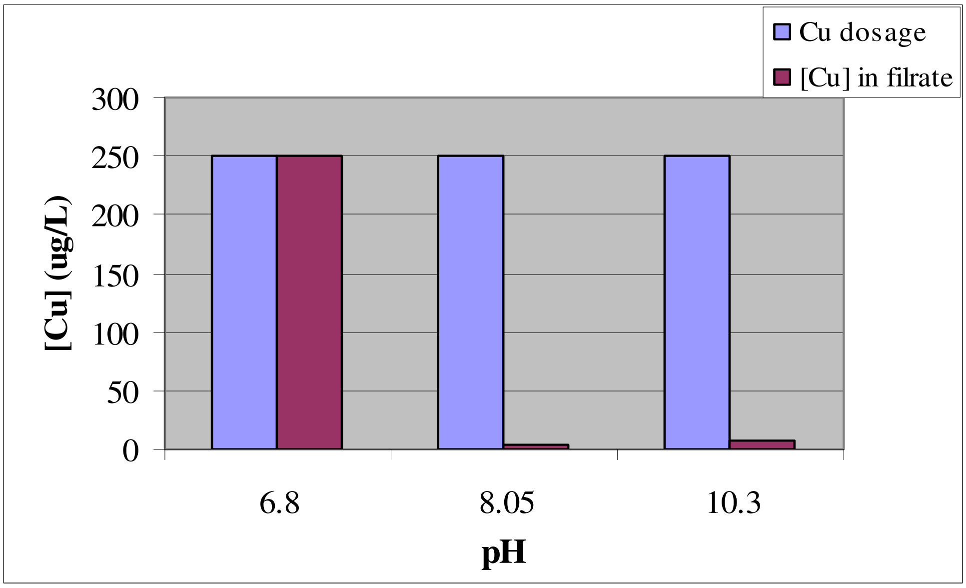

Figure B3 0.2μm PC (Polycarbonate) Membrane Filtration

Note: Cupric sulphate was dosed into deionised water samples at different pH. Various membranes (different pore sizes and materials) were used to filtrate copper hydroxide.

Appendix C

Results of Preliminary Glass Fibre (GF) Filtration Experiments

Table C1 Results of Preliminary GF Filtration of Mundaring Water Sample

Type of Filter	[Cu] (µg/L)	Cu dosage (ug/L)	pH	Description of Filters
MN615	140	300	7.94	Qualitative, ashes contained
MN615+	190	300	7.94	Qualitative, ashes contained
MN1674	200	300	7.94	Quantitative, ashes contained
MN1674+	240	300	7.94	Quantitative, ashes contained
0.45CA	280	300	7.94	0.45um, cellulose acetate
0.2PC	280	300	7.94	0.2um, polycarbonate

Table C2 Results of Preliminary GF Filtration of Deionised Water Sample

Type of Filter	[Cu] (µg/L)	Cu dosage (ug/L)	pH	Description of Filters
MN615	60	310	6.43	Qualitative, ashes contained
MN615+	65	310	6.43	Qualitative, ashes contained
MN1674	14	310	6.43	Quantitative, ashes contained
MN1674+	10	310	6.43	Quantitative, ashes contained
0.45CA	290	310	6.43	0.45um, cellulose acetate
0.2PC	310	310	6.43	0.2um, polycarbonate

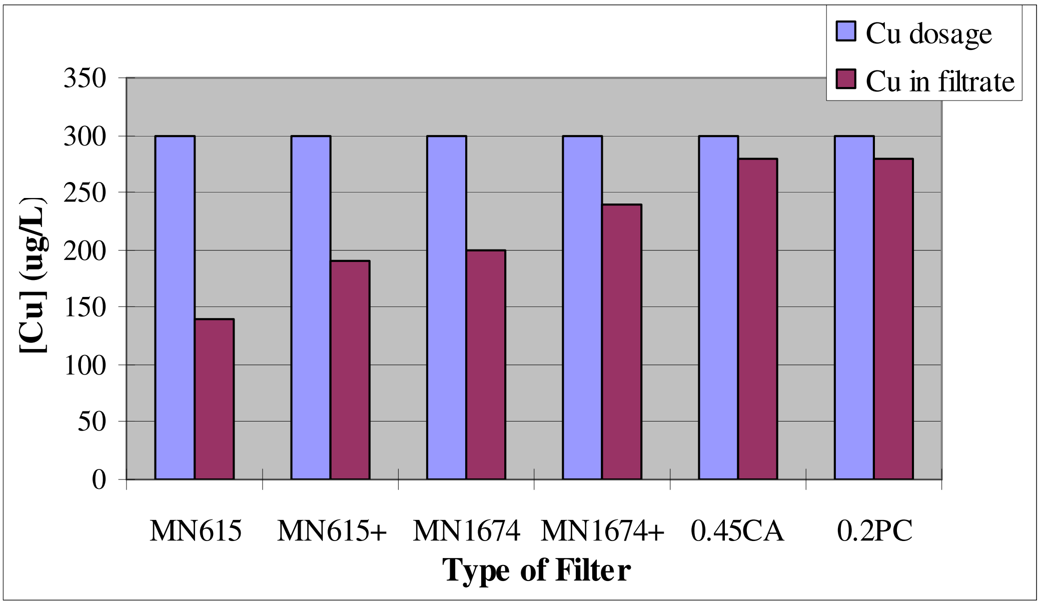

Figure C1 Preliminary GF Filtration of Mundaring Water Sample

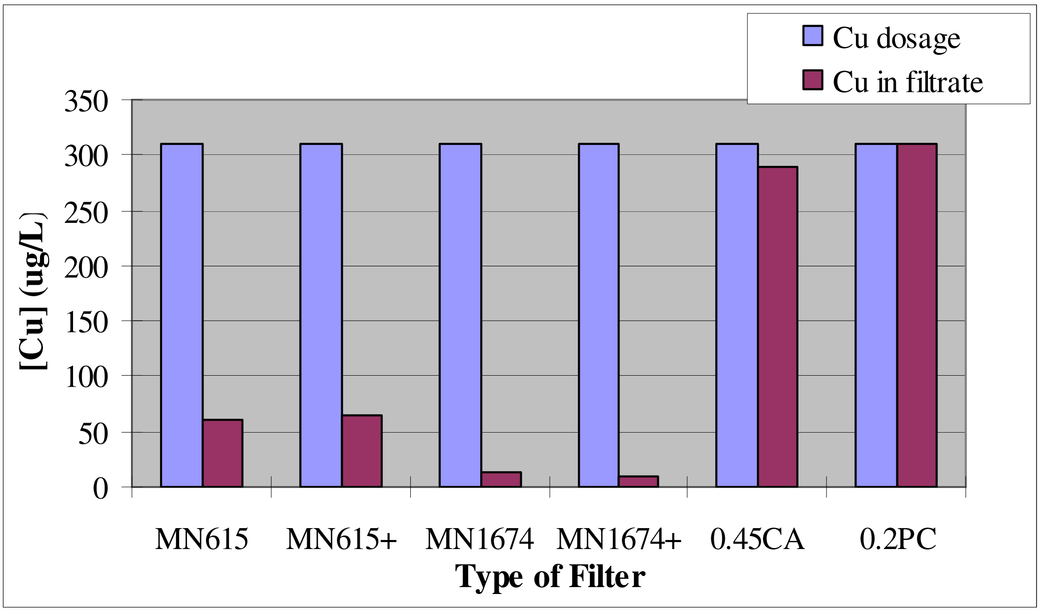

Figure C2 Preliminary GF Filtration of Deionised Water Sample

Appendix D

Results of Field Copper Dosing Experiments

Table D1 Historical Data of Bulk Copper Concentrations in C-K58km along C-K Extension Main Pipeline

Date	Sample Point	Cu Dosage(mg/L)	[Cu](mg/L)	Cu loss (mg/L)
27/04/2006	C-K58km	0.23	0.004	0.226
1/05/2006	C-K58km	0.25	0.02	0.23
2/05/2006	C-K58km	0.23	0.02	0.21
3/05/2006	C-K58km	0.24	0.02	0.22
8/05/2006	C-K58km	0.29	0.02	0.27
18/05/2006	C-K58km	0.24	0.04	0.2
22/05/2006	C-K58km	0.24	0.035	0.205
29/05/2006	C-K58km	0.28	0.04	0.24
8/06/2006	C-K58km	0.32	0.05	0.27
19/06/2006	C-K58km	0.28	0.05	0.23
26/06/2006	C-K58km	0.38	0.05	0.33
3/07/2006	C-K58km	0.41	0.07	0.34
6/07/2006	C-K58km	0.35	0.07	0.28
10/07/2006	C-K58km	0.33	0.02	0.31
9/08/2006	C-K58km	0.3	0.08	0.22
3/01/2007	C-K58km	0.33	0.055	0.275
18/01/2007	C-K58km	0.32	0.06	0.26
31/01/2007	C-K58km	0.24	0.06	0.18
28/02/2007	C-K58km	0.21	0.055	0.155
14/03/2007	C-K58km	0.33	0.07	0.26
27/03/2007	C-K58km	0.32	0.095	0.225
4/04/2007	C-K58km	0.35	0.11	0.24
19/04/2007	C-K58km	0.36	0.095	0.265
2/05/2007	C-K58km	0.36	0.1	0.26
16/05/2007	C-K58km	0.41	0.1	0.31
30/05/2007	C-K58km	0.44	0.15	0.29
26/06/2007	C-K58km	0.42	0.13	0.29
4/07/2007	C-K58km	0.33	0.11	0.22
8/08/2007	C-K58km	0.37	0.12	0.25

Note: “C-K58km” means data was collected from the place which is 58km away from copper dosing point along C-K extension main pipeline.

Table D2 Historical Data of Bulk Copper Concentrations in C-K12.1km along C-K Extension Main Pipeline

Date	Sample Point	Cu Dosage(mg/L)	[Cu](mg/L)	Cu loss(mg/L)
27/04/2006	C-K12.1km	0.23	0.18	0.05
1/05/2006	C-K12.1km	0.25	0.16	0.09
2/05/2006	C-K12.1km	0.23	0.14	0.09
3/05/2006	C-K12.1km	0.24	0.18	0.06
8/05/2006	C-K12.1km	0.29	0.17	0.12
18/05/2006	C-K12.1km	0.24	0.17	0.07
22/05/2006	C-K12.1km	0.24	0.12	0.12
29/05/2006	C-K12.1km	0.28	0.15	0.13
8/06/2006	C-K12.1km	0.32	0.14	0.18
19/06/2006	C-K12.1km	0.28	0.13	0.15
26/06/2006	C-K12.1km	0.38	0.23	0.15
3/07/2006	C-K12.1km	0.41	0.21	0.20
6/07/2006	C-K12.1km	0.35	0.25	0.10
10/07/2006	C-K12.1km	0.33	0.25	0.08
9/08/2006	C-K12.1km	0.3	0.24	0.06

Note: “C-K12.1km” means data was collected from the place which is 12.1km away from copper dosing point along C-K extension main pipeline.