

THE SOUTH AFRICAN OXIDATION AND DISINFECTION MANUAL

Mias van der Walt, Marina Krüger
& Charl van der Walt



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Mias van der Walt, Marina Krüger & Charl van der Walt

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EXECUTIVE SUMMARY

It is always astounding to re-discover the truth: 'There is nothing new under the sun'. It may come as a surprise that our modern society is not the first to think about, or experiment with, water treatment and disinfection, but this is the case. Some Sanskrit¹ writings dating back to earlier than 2000 B.C. offer evidence that water treatment has been practiced by ancient civilizations. It is stated, "*Impure water should be purified by being boiled over a fire, or being heated in the sun, or by dipping a heated iron into it, or it may be purified by filtration through sand and coarse gravel and then allowed to cool.*" In another Sanskrit medical lore reference it is stated, "*It is good to keep water in copper vessels, to expose it to sunlight², and filter through charcoal.*" In the Old Testament³ residents of Jericho confided to Elisha that their city was a pleasant place to live, but the water was causing illness. Elisha responded by throwing in a bowl of salt⁴ into water. In the late 19th century London town officials noticed a decrease in cholera deaths during the 1849 and 1853 epidemics in areas where slow sand filters had been installed. This was followed by the discovery that multiple cholera deaths were linked to sewage contaminated water.

In modern times a whole new perspective on water treatment was developed and concerns arose not only about microbial aspects, but a whole range of chemical substances were identified that polluted drinking water sources. This has led in many parts of the world to the development and continuous revision of water quality legislation, guidelines and rules. In the US, for instance, only a handful of parameters were regulated by the Safe Drinking Water Act in the 1970s. By 2000 more than 150 were listed. The South African guidelines have also seen a number of revisions and the latest South African National Standard (SANS) 241 is currently being finalised.

It is ironic that we are currently experiencing a spate of cholera deaths in Southern Africa in light of the discovery that there is a link between contaminated water and health that was made 150 years ago. These events emphasise the importance, and basic human right, to have access to proper sanitation as well as access to properly disinfected drinking water.

The purpose of the South African Oxidation and Disinfection Manual is to assist the reader in making a logical selection in matching the water treatment challenges with appropriate treatment processes and technology. In order to sensitise the reader to the fact that this selection process is not that simple, a number of chapters were included that address aspects influencing the selection process.

Firstly the reader is introduced to some of the literature available on the subject in Chapter 2. This is followed by a more detailed description of the most commonly found water treatment and distribution system challenges, source characterisation and water quality standards in Chapter 3. A thorough discussion then follows in Chapter 4 on the treatment processes that are available and the relative success in addressing the treatment challenges. Once the process is selected some information is provided on the description of the technology in Chapter 5, occupational health and safety aspects in Chapter 6 and consumer health aspects in Chapter 7. Six case studies were also included in Chapter 8 to demonstrate how water suppliers approached different water treatment challenges.

It should be recognised that the manual does not attempt to be a process design reference, nor a reference on general water treatment principles. It is hoped that this manual can in future be expanded to include the challenges faced by other industries, an expanded process selection methodology and many more case studies.

¹ Letterman, R.B. ed. (1999) Water Quality & Treatment, AWWA

² May this have been the discovery of UV disinfection only to be rediscovered 4000 years later?

³ II Kings 2:19-22

⁴ Could this be an example of sodium chloride disinfection?

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LIST OF ABBREVIATIONS

AOP	Advanced oxidation processes	LT1ESWTR	Long-Term 1 Enhanced Surface Water Treatment Rule
AWWA	American Water Works Association	MCL	Maximum contaminant level
BOD	Biological oxygen demand	MCLG	Maximum contaminant level goal
BS	British Standard	MF	Microfiltration
COD	Chemical oxygen demand	MHI	Major hazardous installation
CPVC	Chlorinated polyvinyl chloride	MP	Medium pressure
CSIR	Council for Science and Industrial Research	MSDS	Material safety data sheet
CT	Concentration contact time	MTBE	Methyl tertiary butyl ether
DAF	Dissolved air flotation	NOM	Natural organic matter
DAFF	Dissolved air flotation and filtration	OEL	Occupational exposure limit
DBP	Disinfection by-product	OHS	Occupational health and safety
DEAT	Department of Environmental Affairs and Tourism	PAC	Powdered activated carbon
DME	Department of Minerals and Energy	PCE	Perchloroethylene
DNA	Deoxyribonucleic acid	PSA	Pressure swing adsorption
DOC	Dissolved organic carbon	RNA	Ribonucleic acid
DWAF	Department of Water Affairs and Forestry	RTD	Residence time distribution
EIA	Environmental impact assessment	SANS	South African National Standard
EPA	Environmental Protection Agency	SDWA	Safe Drinking Water Act (United States)
EPDM	Ethylene propylene diene M-class	SWTR	Surface Water Treatment Rule
EU	European Union	T	Theoretical retention time
GAC	Granular activated carbon	T ₁₀	Residence time of 10% tracer passing outlet of tank
GRP	Glass reinforced plastic	TCE	Trichloroethylene
HAA	Haloacetic acids	TDS	Total dissolved solids
HBA	Hazardous biological agents	THM	Trihalomethane
HCS	Hazardous Chemical Substance	TOC	Total organic carbon
IESWTR	Interim Enhanced Surface Water Treatment Rule	UF	Ultrafiltration
IOA	International Ozone Association	USEPA	United States Environmental Protection Agency
IUVA	International Ultraviolet Association	UV	Ultraviolet (radiation)
IWA	International Water Association	WHO	World Health Organization
LOX	Liquid oxygen	WRC	Water Research Commission
LP	Low pressure	WSP	Water safety plan
LRV	Log removal value	WTW	Water treatment works
LT2SWTR	Long Term Stage 2 Surface Water Treatment Rule	WWTW	Wastewater treatment works

CHAPTER 1 – INTRODUCTION TO THE OXIDATION AND DISINFECTION MANUAL

- 1.1 - Introduction
- 1.2 - Background to development of the manual
- 1.3 - Purpose of the manual
- 1.4 - Overview of the manual
- 1.5 - Guidelines to effective use of the manual

1.1 INTRODUCTION

The Natal Drakensberg is, without a doubt, one of the most beautiful places on earth. In a single day one can experience the full extent of the water cycle. In a few square kilometres the wonders of the natural water cycle unfold with everlasting rhythm. One can touch the clouds formed in front of one's eyes as hot, moist air meets cold mountain air. One can see the beginning of a stream as the clouds empty their watery load onto the mountain slopes. One can also see and drink from small streams and watch these streams uniting into mighty rivers. In the foothills one can see how these rivers plunge down cliffs and calm down in a deep blue pool. Drinking water from such a pristine source is a luxury that is not available to most urban water users.

Every water user in the urban environment impacts in one way or another on the environment through their water use and effluent discharge. Even though the effluent is treated and returned to the streams, it contains substances (pollutants) that can create an imbalance in the natural ecosystem. These imbalances create all kinds of challenges for downstream users that need to re-treat the water for potable use. The urban water use presents many technical as well as cultural challenges. This manual will not attempt to address the cultural and anthropogenic aspects related to water use, but will provide some technical guidelines to treatment of different types of water.

The increased pollution and re-use of water increasingly expose water users to substances in the water that may not be effectively removed by conventional treatment processes and require additional and advanced treatment. The manual attempts to give some guidance towards making informed decisions with regard to various oxidation and disinfection unit processes as part of the total water treatment process.

1.2 BACKGROUND TO DEVELOPMENT OF THE MANUAL

In 2006, a group of people identified the need to share knowledge on specific disinfection technology. The group was expanded and it was soon realised that the need for sharing this knowledge was much greater than originally anticipated. A number of disinfection failures in the water supply systems had emphasised the importance of sharing knowledge on oxidation and disinfection technology. It was also felt at the time that South Africa faced a number of unique water treatment challenges. The manual was developed for the South African context. In 2007 a motivation was submitted to the WRC to fund the development of such a manual. The funds were approved in September 2007.

1.3 PURPOSE OF THE MANUAL

The purpose of the manual is to provide a basic and practical introduction to oxidation and disinfection with sections on the theoretical background, oxidation and disinfection processes and oxidation and disinfection technology available. Case studies of how the processes and technology were applied were also included to provide practical examples for the users of the manual.

It should be recognised that the manual does not attempt to be a process design reference, nor a reference on general water treatment principles. The manual addresses only two unit treatment processes commonly found in the water treatment process trains, i.e. oxidation and disinfection. For a more detailed and comprehensive description of the processes referred to in this manual the reader is referred to the vast amount of literature available on these subjects, some of which is listed in Chapter 2.

1.4 OVERVIEW OF THE MANUAL

The manual takes a practical approach and is divided into the following chapters:

- Chapter 2 explores some of the literature available.
- Chapter 3 describes water source characterisation, treatment objectives and standards.
- Chapter 4 provides technical details of oxidation and disinfection processes.
- Chapter 5 describes oxidation and disinfection technology.
- Chapter 6 describes consumer health related aspects.
- Chapter 7 covers occupational health and safety aspects.
- Chapter 8 contains a number of case studies.

1.5 GUIDELINES TO EFFECTIVE USE OF THE MANUAL

The manual has been structured in such a manner that it can be used by readers with varying levels of knowledge of oxidation and disinfection, and it features:

- A basic theoretical reference to oxidation and disinfection processes.
- A chart for initial selection of suitable processes for a number of typical water treatment challenges.
- A description of oxidation and disinfection technology.
- Case studies from which readers can learn how technology was used in meeting water treatment challenges.

CHAPTER 2 – LITERATURE RESEARCH

- 2.1 - Introduction
- 2.2 - International associations, agencies and suppliers
- 2.3 - National associates and government department

2.1 INTRODUCTION

No manual will be complete without an overview of the available literature on the subject. In recent times information is more readily available by means of the Internet. An Internet search engine such as Google can provide thousands of hits on a particular subject. Unfortunately, the information is often presented in a format that may be of little use to the novice unless the search criteria were posed correctly. In addition, the information also needs to be considered in the context in which it was presented. For this reason it is often better to direct a literature search towards professional organisations that have developed quality reference material on the subject over many years. The literature research therefore focused on reference material that is available from internationally recognised professional associations, suppliers and consultants. A number of these references are discussed below. It should also be noted that the intention was not to summarise the literature, but simply to direct the reader to potential sources.

2.2 INTERNATIONAL ASSOCIATIONS, AGENCIES AND SUPPLIERS

2.2.1 UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

The United States Environmental Protection Agency (USEPA) has generated reference material on a wide range of water and wastewater related subjects, including oxidation and disinfection, over a number of decades. Many of the guidelines can be accessed online from the USEPA website (www.epa.gov). Of particular interest are the USEPA guidelines and regulations that were developed as part of the Safe Drinking Water Act (SDWA). Some of the recent guidelines include practical advice on the implementation of the Surface Water Treatment Rule. The USEPA has also developed specific guidelines with respect to oxidation and disinfection in meeting the requirements published under the SDWA. One of the manuals developed by USEPA that is of particular relevance and that was consulted extensively in the development of this manual is the *Alternative Disinfectants and Oxidants Guidance Manual* (USEPA, 1999).

2.2.2 American Water Works Association (AWWA) and AWWA Research Foundation

The American Water Works Association (AWWA) is a professional association that has developed an enormous library of reference material over many years. The AWWA also publishes a monthly journal, *Journal of the American Water Works Association* and a practical journal, *Opflow*, which provides information on recent developments in research and technology. The reference material published by AWWA can be ordered online from the AWWA bookshop website (www.awwa.org/bookstore) and includes the following categories:

- Best Practice Manuals, M-series
- AWWA standards
- Specialist research reports published by AWWA Research Foundation
- Books on selected subjects
- Video material on a range of subjects

2.2.2.1 *Water Treatment Plant Design*

A particular useful publication is *Water Treatment Plant Design* (AWWA and ASCE, 2005), a classic reference for all design engineers. This publication features a chapter on oxidation and disinfection which deals with the regulatory framework, chemical oxidation treatment, chlorination, chlorine dioxide systems and ozone disinfection systems. A special chapter is dedicated to ultraviolet disinfection (UV) and covers principles of UV disinfection, applications for UV disinfection, UV disinfection equipment, water quality and treatment effects on UV disinfection, UV disinfection facility planning, design and project implementation construction, testing, start-up, operation and maintenance, potential regulatory requirements for UV disinfection in North America and validation testing. Some of the other recent relevant publications are discussed below.

2.2.2.2 *Waterborne Pathogens*

The new edition of *Waterborne Pathogens* (AWWA, 2006a) provides information required to detect and eliminate waterborne pathogens in drinking water. It covers everything water utility managers, lab workers, and operators need to know about waterborne microbial pathogens, new and emerging microbial pathogens, improved detection methods, best treatment practice for killing or removing many types of waterborne pathogens, water quality monitoring methods, sampling techniques, testing procedures and waterborne outbreak statistics.

2.2.2.3 *Water Chlorination / Chloramination Practice and Principles*

The *Water Chlorination / Chloramination Practices and Principles* manual (AWWA, 2006b) is a complete information resource on the uses of chlorine and chloramines in water treatment. Beginning with a brief history of these important chemicals, the manual focuses on their chemical properties and disinfection mechanisms; proper handling, storage and safety techniques; feed equipment types and ancillary equipment; chlorine and chloramine disinfection strategies and techniques to minimise the formation of disinfection by-products (DBPs) while maintaining adequate disinfection and distribution system residuals.

2.2.2.4 *Fundamentals and Control of Nitrification in Chloraminated Drinking Water Distribution Systems*

The *Fundamentals and Control of Nitrification in Chloraminated Drinking Water Distribution Systems Manual* (AWWA, 2006c) provides information on prevention, treatment, monitoring and control of nitrification. It identifies the causes of nitrification in chloraminated systems, health impacts, growth and inactivation of bacteria, operational response to an episode, and system improvements to prevent nitrification.

2.2.2.5 *Handbook of Chlorination and Alternative Disinfectants*

The *Handbook of Chlorination and Alternative Disinfectants* (White, 1998) is a complete reference on the use of types of water disinfectants: chlorine, chlorine dioxide, ozone, peroxone, bromine, bromine chloride, iodine and ultraviolet radiation in potable water production and wastewater treatment. The handbook covers aspects such as chemistry, effectiveness, dosing, facility design and equipment for each of these disinfectants. It is a practical, user-friendly operations manual and technical reference for water and wastewater operators, water regulatory agencies, and process engineers.

2.2.2.6 *Water Quality and Treatment: a Handbook of Community Water Supplies*

Water Quality and Treatment: A Handbook of Community Water Supplies (AWWA, 1999) is a renowned text and a complete resource on drinking water quality and treatment. It explains all conventional and alternative treatment processes.

2.2.2.7 *Chemistry of Water Treatment*

This popular professional reference and teaching text (Faust and Aly, 1998) contains the information required to select the correct treatment processes for specific raw water characteristics and assure compliance with governmental requirements. The text is organised by contaminant and by treatment process, so one can go directly to the chapter that covers the contaminant of interest and its removal. It covers particulate matter, corrosive substances, pathogens, organic substances, inorganic substances, chemicals, scale-forming substances, and a range of other water contaminants.

2.2.2.8 *Ozone in Drinking Water Treatment: Process Design, Operation, and Optimisation*

Ozone in Drinking Water Treatment: Process Design, Operation, and Optimisation (Rakness, 2005) offers insight and technical expertise in the use of ozone in drinking water treatment. This reference is intended to serve as a primary information resource for those wishing to design, operate, maintain, control and optimise ozone technology in drinking water treatment. The author provides an operations perspective, based on his experience in the design, start-up and operation of more than 50 ozone treatment facilities. Filled with practical advice and information that can be put to immediate use, the book has dozens of figures illustrating ozone equipment and installations. Many tables provide data on ozone's effectiveness against *Cryptosporidium* and other contaminants, and on optimising ozone treatment to achieve the best results at the lowest costs.

2.2.2.9 *Water Treatment Principles and Design*

Water Treatment Principles and Design (MWH, 2005) is a single volume information resource for water treatment operators, utility managers and plant designers on conventional and advanced water treatment design and operation. This handbook provides theory, design and operational information for all conventional water treatment plant processes, plus advanced processes such as membrane filtration. It offers treatment options for all organic and inorganic contaminants, disposal of treatment plant residuals and taste and odour problems. Problems, discussion topics and references are included at the end of each chapter, making this text ideal for classroom use.

2.2.2.10 *Biodegradable Organic Matter in Drinking Water Treatment and Distribution*

Biodegradable Organic Matter in Drinking Water: Water Treatment and Distribution (CPWSDS:ARR and NRC, 2006a) provides a wealth of information on the subject. Biodegradable organic matter can degrade water quality at the consumer's tap, cause taste and odour complaints and result in regulatory violations. The reader will understand the nature of biodegradable organic matter, how it can affect water quality and what treatment options are available.

2.2.2.11 *Drinking Water Distribution Systems: Assessing and Reducing Risks*

The USEPA has renewed its interest in water quality degradation occurring during distribution, with the goal of defining the extent of the problem and considering how it can be addressed via both regulatory and non-regulatory channels. The Agency requested the National Academies Water Science and Technology Board to conduct a study of water quality issues associated with public water supply distribution systems and their potential risks to consumers. *Drinking Water Distribution Systems: Assessing and Reducing Risks* (CPWSDS:ARR and NRC, 2006b) provides the results of the study.

2.2.2.12 *Modeling Water Quality in Drinking Water Distribution Systems*

Water quality modelling is a powerful tool for drinking water utilities of all sizes to help understand the factors that affect water quality in the distribution system. This publication (Clark and Grayman, 1998) will provide information on how to develop water quality modelling systems and how to model total trihalomethanes, chlorine decay, waterborne disease outbreaks, the effects of tanks and storage on water quality and many other aspects of water quality.

2.2.2.13 *Water Quality in the Distribution System*

This book is designed to be the water professional's primary resource on the subject of water quality in the distribution system. The reference (Lauer, 2005) is divided into nine major sections: introduction, microbiological issues, chemical and physical issues, chloramine conversion issues, corrosion control, rapid or real-time monitoring, operational practices, flushing to maintain water quality, and water quality computer modelling.

2.2.2.14 *Disinfection of Pipelines and Storage Facilities Field Guide*

This field guide (Lauer and Sanchez, 2006) for use by water system workers provides proper procedures for preventing microbial contamination of water mains, storage tanks and other distribution system components, post-installation disinfection, testing, flushing and dechlorination.

2.2.2.15 *Comprehensive Water Distribution Systems Analysis Handbook for Engineers and Planners*

Simulation and analysis of water quality in distribution systems are vital in giving the reader a better understanding of the dynamics of water quality variations, the complex processes that take place in the distribution system environment and the ways in which these vulnerabilities impact on system performance and safety. This handbook (Lansey and Boulos, 2005) presents a comprehensive discussion on the theoretical and practical aspects of water quality analysis in potable water distribution systems from steady state equilibrium to sophisticated dynamic analysis techniques for complex networks of pipes, tanks, reservoirs and junctions.

2.2.2.16 *Wastewater Engineering: Treatment and Reuse*

As the industry's leading professional reference on wastewater, this book by Metcalf & Eddy Inc. *et al.* (2002) provides the most current information on all aspects of modern wastewater engineering. The publication provides information on oxidation and disinfection for wastewater and water re-use applications including: advanced oxidation processes (AOPs), disinfection with chlorine dioxide, characteristics of chlorine dioxide chlorination and dechlorination, ozone disinfection, paracetic acid,

hydrogen peroxide, peroxone and also provides a useful comparison of alternative disinfection technologies.

2.2.2.17 *Water Supply Operations*

The *Principles and Practices of Water Supply Operations* series by AWWA comprises five parts:

- I) *Water Sources* (AWWA, 2003a)
- II) *Water Treatment* (AWWA, 2003b)
- III) *Water Transmission and Distribution* (AWWA, 2003c)
- IV) *Water Quality* (AWWA, 2003d)
- V) *Basic Science Concepts and Applications* (AWWA, 2003e)

The two most relevant parts in this series for oxidation and disinfection are *Part II: Water Treatment* (AWWA, 2003b) and *Part III: Water Transmission and Distribution* (AWWA, 2003c). These volumes introduce the fundamentals of drinking water treatment processes. Specific topics include raw water quality, treatment options, treatment chemicals and drinking water regulations. The chapters discuss specific treatment processes in detail. The text also examines common operation problems and solutions. The basics of design, construction, operation and maintenance of water transmission and distribution systems are presented in this introductory text. It examines individual system components, cross-connections and backflow prevention.

2.2.2.18 *Integrated Design and Operation of Water Treatment Facilities*

Kawamura (2000) provides practical guidelines on a number of aspects including general disinfection processes considerations and alternative disinfectants such as chloramines, chlorine dioxide, ozone and ultraviolet light. The author also provides useful design criteria and example design calculations as well as operation and maintenance considerations.

A number of chapters deal with specialised aspects on ozonation systems, iron and manganese removal, taste and odour control and DBP control. Each specialised chapter deals with design considerations, design criteria, example design calculations and operation and maintenance considerations. The chapter on taste and odour control also includes a section on major taste- and odour-producing substances as well as control measures at the treatment plant and the distribution system.

2.2.2.19 AWWA Research Foundation

The AWWA Research Foundation published a range of research manuals relating to the field of disinfection and oxidation, among them are:

- Practical Taste and Odour Methods for Routine Operations
- Distribution System Security Primer for Water Utilities
- Development of Distribution System Water Quality Optimisation Plans
- Ozone-enhanced Biofiltration for Geosmin and MIB Removal
- Impact of Chlorine Dioxide on Transmission, Treatment and Distribution System Performance
- Impact of Distribution System Water Quality on Disinfection Efficiency
- Early Warning and Management of Surface Water Taste and Odour Events
- Formation and Decay of Disinfection By-Products in the Distribution System
- Organic Nitrogen in Drinking Water and Reclaimed Wastewater
- Managing Distribution Retention Time to Improve Water Quality - Phase 2: Guidance Manual
- Assessment of Chloramine and Chlorine Residual Decay in the Distribution System

- Application of HACCP for Distribution System Protection
- Seasonal Chlorination Practices and Impacts to Chloramination Utilities
- Distribution Water Quality Issues related to New Development or Low Usage
- Addressing Concerns About Taste and Odours and Cyanotoxins in Tap Water
- Treatment of Water with Elevated Organic Content
- Monitoring Ammonia-Oxidising Bacteria in Chloraminated Distribution Systems

These and all AWWA publications are available from AWWA by ordering online at www.awwa.org/bookstore or phoning AWWA Customer Service on 001 303 794 7711.

2.2.3 International Water Association

The International Water Association (IWA) publishes journals with articles on a large variety of water and wastewater related subjects. They also publish a number of specialist journals that provide a plethora of information on all aspects relating to water treatment including oxidation and disinfection. The journals can only be accessed by members registered to receive the manuals. In addition to these journals, IWA also publishes reference material on a wide range of subjects. Some of the recent publications include:

2.2.3.1 *Journal of Water and Health*

This journal (www.iwapublishing.com/jwh) is informative on the health implications and the control of waterborne micro-organisms. This includes microbial toxins, chemical quality and the aesthetic qualities of water. It covers the following health-related aspects: epidemiology, risk assessment, water and wastewater treatment, disinfection, DBPs, indicators of water and waste quality, regulatory issues and standard development water quality surveys, endocrine disruptors and taste and odour.

2.2.3.2 *Journal of Water Supply: Research and Technology – AQUA*

Aqua is a peer-reviewed scientific and technical journal (www.iwapublishing.com/jws) with practical/operational papers focusing on the research and development in water supply technology and management. It covers aspects like water treatment processes, residuals treatment and management, modelling of source waters, treatment and distribution systems, applied methods to characterise water quality distribution systems, water system management and policy – legislation, economics, public relations, crises management, public health, risk assessment and regulations and standards.

2.2.3.3 *Water Research*

Water Research (www.iwapublishing.com/wr) publishes refereed, original research papers covering the aspects of science and technology of water quality and the management thereof, worldwide. The topics include treatment processes of water and wastewaters and water quality standards.

2.2.3.4 *Water Science and Technology*

Water Science and Technology (www.iwapublishing.com/wst) publishes peer-reviewed papers on all aspects of science and technology of water pollution control and water quality management worldwide. Some areas covered include wastewater treatment and transportation processes for storm water and domestic, industrial and municipal effluents and effects and impacts of pollution on rivers, lakes, groundwater and marine water.

2.2.3.5 *Water Science and Technology: Water Supply*

Water Science and Technology: Water Supply (www.iwapublishing.com/ws) publishes the best papers admitted on all aspects of water supply. The topics include water treatment technologies, wastewater, water distribution systems, drinking water quality and water pollutants, characteristics and effects.

2.2.3.6 *Risk Management for Water and Wastewater Utilities*

The IWA is promoting a risk-based approach to water utility management, from catchment to tap, through the implementation of the Bonn Charter. With this in mind, this book by Pollard (2008) contains unit processes and process reliability to begin with, and then broadens out to consider first environmental and then organisational risk management. The final sections are concerned with better utility decision-making. The book has been designed for self-paced study, giving step-by-step learning in a particular subject including exercises and self-assessment questions to test your understanding, as well as text references.

2.2.4 International Ozone Association

Where USEPA, AWWA and IWA provide information on a wide range of subjects, the International Ozone Association (IOA) focuses on ozone application. The IOA has an official monthly journal that generates up to date research on matters relating to ozone applications. The journal is accessible to registered members. The association website is www.io3a.org.

2.2.5 International Ultraviolet Association

The International Ultraviolet Association (IUVA) is another specialised professional association (www.iuva.org). Similar to IOA, IUVA also provides publications on the specialised subject of UV disinfection.

2.2.6 Degrémont Suez

The *Degrémont Suez Water Treatment Handbook* (Degrémont Suez, 2007) provides a wide range of theoretical knowledge as well as case studies where their technology was applied. Chapter 3 deals with fundamental physical-chemical engineering processes applicable to water treatment and includes the following on oxidation and reduction theory: oxidation-reduction reactions, fundamental concepts on the oxidation-reduction chemical reaction, basic concepts on disinfection, various oxidants and disinfectants including oxygen, chlorine and hypochlorite, chlorine dioxide, ozone, potassium permanganate, hydrogen peroxide, peracetic acid, UV radiation and several advanced oxidation systems.

Chapter 17 deals with oxidation and disinfection technology and addresses different processes such as chlorine dioxide, ozone, potassium permanganate, bromium, hydrogen peroxide, peracetic acid and ultraviolet disinfection. The manual also provides useful information on the various types of reactors used in drinking water applications, wastewater applications and industrial water applications.

2.3 NATIONAL ASSOCIATES AND GOVERNMENT DEPARTMENTS

2.3.1 Water Research Commission of South Africa

The Water Research Commission (WRC) of South Africa is a government-funded organisation that was established to conduct water research related activities. The WRC has published a large number of research reports, guidelines and manuals on a variety of water related aspects. Interested readers can visit the WRC website (www.wrc.org.za) for a list of the publications. Most of the publications are available in hard copy format from the WRC offices in Pretoria. Orders should be sent by e-mail to the Publications Department: orders@wrc.org.za. When placing an order, always include the Report Number given on the Research Category list. Most of the publications are available at no charge to South African citizens, although normal postage rates will apply for orders weighing more than 3 kg. Local and/or international costs are indicated for individual publications (where applicable) on the Research Category lists.

2.3.2 Department of Water Affairs and Forestry

The Department of Water Affairs and Forestry (DWAF, www.dwaf.gov.za) as the custodian of water resources in South Africa, has played a significant role in the effort to make safe potable water available to all South Africans. As a result they have developed a number of guidelines to assist Water Services Authorities and Water Services Providers in meeting their constitutional obligations. Publications can be downloaded from the DWAF website. The most relevant publications developed by DWAF on the subject of this manual are the Water Quality Guidelines. These guidelines comprise a number of volumes and explain the health effects of various substances in the water, sampling requirements, basic treatment requirements and management aspects.

Another very useful DWAF publication that was recently issued is the Best Practice Guidelines on Integrated Mine Water Management. This set of manuals addresses many aspects relating to mine water impact, management, treatment, and monitoring.

2.3.3 Other sources of information

Various other institutions have also contributed in many ways to the knowledge pool of oxidation and disinfection processes. Unfortunately, not all the information is available in the public domain, but only as internal research reports. The organisations include the Council for Scientific and Industrial Research (CSIR), Mintek, universities, water boards and some larger municipalities.

CHAPTER 3 – WATER CHARACTERISATION AND STANDARDS

- 3.1 - Introduction
- 3.2 - Three key steps
- 3.3 - Water source characterisation
- 3.4 - Water quality standards
- 3.5 - Industry challenges and treatment objectives
- 3.6 - Introduction to the selection chart

3.1 INTRODUCTION

This chapter provides some basic information on how water characterisation can be used to facilitate the selection of appropriate oxidation and disinfection processes to meet water quality standards applicable to the particular application. It will be demonstrated how this knowledge can be used to meet some of the typical water treatment challenges. It should be noted that this chapter does not pretend to be an exhaustive process design guideline, but only attempts to improve the reader's basic understanding of water characterisation and the need for it. It is recommended that the services of a professional water treatment specialist be acquired to perform a comprehensive process design. This chapter also aims at raising the awareness of the reader on certain key decisions that need to be taken when assessing the water treatment needs. The subject of process design is beyond the scope of this manual and the reader is referred to the literature cited in Chapter 2 for more detail.

3.2 THREE KEY STEPS

Before an oxidation and/or disinfection process can be selected, it is essential to consider the following three key steps:

- **Firstly**, the nature of the water that requires treatment needs to be understood. This process is generally referred to as water source *characterisation* and is described in more detail in section 3.3.
- **Secondly**, once the water quality of the source has been characterised the ultimate treated water *objectives*, as regulated by an appropriate *standard*, need to be developed. A selection of water quality standards is discussed in more detail in section 3.4.
- **Thirdly**, the appropriate unit processes required to meet the (oxidation and disinfection) treatment objectives and standards need to be selected. This step is often an iterative process and involves many different selection criteria to determine the most cost-effective treatment train. It should be noted that the oxidation and disinfection unit processes discussed in the manual are only a selection of a process that will form part of the complete treatment train. Section 3.5 describes how the typical treatment challenges can be addressed, using conventional and advanced oxidation and disinfection processes.

3.3 WATER SOURCE CHARACTERISATION

The characterisation of a water source is probably one of the most important steps in the design of any water treatment plant. If the quality of water source is not known, it is unlikely that an appropriate treatment process will be selected and the treatment objectives will not be reached.

Water quality data required should typically include the parameters regulated by the appropriate water quality standard. In some cases it may also be necessary to assess parameters not required by the particular water quality standard if knowledge of the origin of the water exists. For instance, the

SANS 241 potable water quality standard is silent on the nature of the organic material in the water. A highly polluted water of sewage effluent origin that needs to be treated to potable standards should, if possible, also be screened for the occurrence of known organic pollutants.

It is essential that a number of complete sets of water quality data be obtained to identify the water type, the particular water quality issues that were identified and the variation of individual water quality parameters over a specific period. In most cases, a sampling program will have to be initiated in order to collect sufficient data to ensure a proper source water characterisation.

In most cases insufficient data are available to perform a proper source water characterisation. Data sources available to the public often provide only information on selected bacteriological, physical and metal content. Very few data sources include sufficient information on key parameters required for the selection of oxidation and disinfection processes or the entire process train.

3.3.1 Source water categories for potable treatment purposes

In South Africa a number of source water categories can be distinguished, based on the quality of the water. Typical parameters that are used to categorise the source include: turbidity, colour, ammonia, hardness, trophic state and dissolved metal content. The source can also be categorised in terms of its origin and its associated level of variability.

In South Africa water quality abstracted from a river can be expected to vary more than water abstracted from a dam (reservoir). The area in which the dam is located will also determine the character of the water. A dam located downstream of a large town can be expected to present high levels of eutrophication and all the associated challenges such as high concentrations of ammonia and/or nitrate, high algal cell counts, high dissolved organic carbon (DOC) content and in some cases even taste and odour problems and algal toxins.

Water quality from a borehole is to a large extent determined by the geology of the area in which the borehole is located and the extent of surface infiltration. Borehole water quality can be expected to vary less than surface water quality, but significant differences between boreholes in the same area are possible.

The reader shall note that many exceptions exist to the general categories described. It is therefore essential that the special challenges of each source are identified through a thorough sampling and analysis program. Section 3.5 lists the most commonly found water treatment challenges.

3.3.2 Source water categories for wastewater and industrial treatment purposes

The quantity and quality of effluent from a wastewater treatment works (WWTW) will depend on the community and industry feeding the specific wastewater treatment system. The effluent quality will also depend on which standard is applicable to the WWTW and the level of compliance to the standard. Water quality data of effluent from existing wastewater treatment plants should be available as it is regulated by the National Water Act. For the case of new wastewater treatment plants, assumptions will have to be made with regard to the expected waste character based on the population demographics and industrial activities.

The effluent from mines and industries will vary depending on the mining and industrial activities and production processes employed. Each mine and industry will have its own particular treatment challenge and this can only be determined for a specific site and from a detailed sampling and analysis program. Section 3.5 lists the most commonly found industrial water treatment challenges.

3.4 WATER QUALITY STANDARDS

3.4.1 Drinking water standards

A variety of water quality standards are used throughout the world. The standards are continuously reviewed, updated and refined as new pollutants are identified and new toxicological evidence requires the revision of exposure levels of known substances. Some of the most common internationally recognised drinking water standards include:

- South African National Standard (SANS) 241, *Drinking Water* (SANS 214:2006 at time of going to press, but consult the most recent version of the standard). All South African National Standards are available from the South African Bureau of Standards offline by phoning 012 428 6883 or on the internet at <https://www.sabs.co.za/index.php?page=standardspurchase>.
- The World Health Organization's *Guidelines for Drinking-Water Quality* (WHO, 2008). At the time of writing, this document was available online for free download from the WHO's website, at www.who.int/water_sanitation_health/dwq/gdwq3rev/en/index.html. However, the link changes from time to time and in that case the reader may find the document by searching the WHO's main website, www.who.int.
- The USEPA standards are available from www.epa.gov/safewater. There are two categories of drinking water standards:

A National Primary Drinking Water Regulation (NPDWR or primary standard) is a legally-enforceable standard that applies to public water systems. Primary standards protect drinking water quality by limiting the levels of specific contaminants that can adversely affect public health and are known or anticipated to occur in water. They take the form of Maximum Contaminant Levels or Treatment Techniques, which are described below.

A National Secondary Drinking Water Regulation (NSDWR or secondary standard) is a non-enforceable guideline regarding contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odour, or colour) in drinking water. The USEPA recommends secondary standards to water systems but does not require systems to comply. However, states may choose to adopt them as enforceable standards. This information focuses on national primary standards.

The most relevant USEPA standards to this topic are *Microbials, Disinfectants, and Disinfection Byproducts*, which incorporate nine rules and which may be freely downloaded from the USEPA website at www.epa.gov/safewater/disinfection/index.html.

- BS/ISO Standards can be obtained from www.bsi-global.com/Standards-and-Publications/ and include, for example, *BS EN 14718:2006 BS EN 14718:2006. Influence of organic materials on water intended for human consumption. Determination of the chlorine demand. Test method.*
- Australian standards, available from the Cooperative Research Centre for Water Quality and Treatment (www.waterquality.crc.org.au).

Only two standards will be discussed in detail, the local SANS 241:2006 standard and the USEPA standard. The USEPA standard is discussed as it is one of the most dynamic standards and is often updated with new regulations, parameters and compliance levels.

3.4.1.1 South African National Standard 241 water quality standard

South African National Standard 241:2006 features a two-tier water quality standard. Class 1 and Class 2 are distinguished by their allowable long- and short-term exposure. The frequency of compliance to these standards is also specified. An alert level was also introduced for the purpose of alarming users, should short term operational problems be experienced, in particular with regard to disinfection effectiveness. The SANS 241 document is also prescriptive in terms of the frequency of sampling based on the size of population served. An essential part of SANS 241 is the requirement to perform a risk assessment and the development of a water safety plan when compiling a water quality sampling program. A revision of SANS 241 is planned for release in 2009 and as the 2009 version contains significant changes (e.g. the removal of the class I and II system, the inclusion of Blue Drop Green Drop certification and the compulsory inclusion of Water Safety Plans) the reader is strongly urged to obtain a copy of the document when it becomes available.

The Department of Water Affairs and Forestry has published an eight-volume manual (*South African Water Quality Guidelines*) explaining the nature of, and the reason for, monitoring each parameter regulated by SANS 241.

3.4.1.2 United States Environmental Protection Agency

The USEPA standard is comprehensive and differs considerably from the SANS 241 approach. The USEPA regulates the maximum allowable level of a vast number of parameters similar to SANS 241, but in cases where it is not cost effective to determine the concentration of a particular water quality parameter, a treatment process (treatment rule) is prescribed. One example of such a requirement has been extracted from the USEPA standard and is shown as Table 1.

Table 1 – Primary drinking water regulations related to microbiological contaminants (adapted from USEPA, 1999)

Compound	MCLG (mg/L)	MCL (mg/L)	Potential Health Effects	Sources of Drinking Water Contamination
<i>Giardia lamblia</i>	Zero	TT ¹	Gastro-enteric disease	Human and animal faecal waste
<i>Legionella</i> spp.	Zero	TT	Legionnaire's disease	Common bacteria in natural waters; can proliferate in water heating systems
Heterotrophic plate count	N/Z	TT	Indicates water quality, effectiveness of treatment	
Total coliforms	Zero	<5.0% ²	Indicates potential presence of gastro-enteric pathogens	Human and animal faecal waste
Turbidity	N/A	TT	Indicates water treatment failure and pathogens in drinking water	Particles from storm runoff, discharges into source water and erosion
Viruses	Zero	TT	Gastro-enteric disease	

- ¹TT = Treatment technique requirement in lieu of MCL
- ²No more than 5% positive if >40 samples/month; no more than 1% positive if <40 samples/month
- MCLG: Maximum Contaminant Level Goal
- MCL: Maximum Contaminant Level

This approach has been phased in over a number of years with different treatment objectives addressed by each specific treatment rule. The latest in a series of treatment rules is the Long Term Stage 2 Surface Water Treatment Rule (LT2SWTR). This rule describes particular requirements for the disinfection of *Giardia* and *Cryptosporidium*. Other treatment rules include:

- The stage 1 Disinfectants and Disinfection By-products Rule (DBPR)
- Interim Enhanced Surface Water Treatment Rule (IESWTR)
- Long-Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR)
- Ground Water Rule (GWR)
- Filter Backwash Rule (FBR)

3.4.2 Municipal wastewater and industrial standards

Wastewater standards are regulated based on environmental and health impacts, and vary considerably across the world. New wastewater works will require a comprehensive environmental impact assessment (EIA). In South Africa effluent from wastewater treatment plants need to comply with either the General Standard or the Special Standard for effluent as set by DWAF (1999). A discharge permit is also issued in which site-specific requirements are detailed. More recently DWAF initiated a process where an integrated water use license is required for all water use related activities in a municipal area or an industrial user such as a mine. An example of the requirements of a Special Standard effluent permit is shown in Table 2. The contents of a Special Standard will depend on the sensitivity of the river system/catchment into which the effluent is discharged.

Table 2 – Example of Special Standard Effluent Quality

Parameter		Limit
pH		6.5-8.5
Electrical conductivity	(at 20°C)	≤ 80 mS/m
Nitrate	(as N)	≤ 6 mg/L
Free and saline ammonia	(as N)	≤ 1 mg/L
Chemical oxygen demand	(as O)	≤ 50 mg/L
Orthophosphate	(as P)	≤ 0.9 mg/L
Suspended solid		≤ 10 mg/L
Free residual chlorine	(as Cl)	≤ 0.2 µg/L
Faecal coliforms		≤ 150 CFU/100 mL

Most of the treatment processes employed for municipal wastewater treatment involve biological nutrient removal processes such as nitrification and de-nitrification. Chemical oxidation is generally not practiced. Disinfection is often practiced at the end of the biological treatment process and reserved to reduce the level of faecal coliform bacteria. There is currently no standard in South Africa regulating the pathogenic parasite levels such as *Giardia* and *Cryptosporidium* from municipal wastewater treatment plants. The guidelines and standards pertaining to the design of effective disinfection of treated municipal wastewater has not been developed to the same level compared to that available for potable water treatment. This is probably an area where much more attention will be focused in the future with the increasing level of direct and indirect re-use of sewage effluent.

Standards applicable to industrial and mining water are regulated either by the particular municipal bylaws and/or by the requirements of the Constitution of the Republic of South Africa, National Water Act, National Environmental Management Act, Minerals and Petroleum Resources Act, National Environment Management: Air Quality Act or the Environment Conservation Act. The standard applicable to a particular industry or mine is often a negotiated process between the regulator (Department of Water and Environmental Affairs (DWEA)), the Department of Mining (DoM) and the water user. In most cases mines are required to implement a zero discharge policy with recycling of process water and final disposal in lined slime dams. Industrial wastewater is allowed to be discharged into municipal sewer systems only after being treated to minimum quality requirements and then further treated at the municipal wastewater works.

The specific requirements are case-dependent and subject to a more in-depth understanding of the particular manufacturing processes and waste streams. After analysing the waste streams an appropriate process design can be performed. The typical challenges faced by, for instance the mining industry, have recently been described in a series of best practice guidelines published by DWAF (2008).

3.5 INDUSTRY CHALLENGES AND TREATMENT OBJECTIVES

The treatment objectives of each industry vary considerably and are discussed in two separate sections – one for potable water and one for municipal and industrial wastewater.

3.5.1 Potable water treatment challenges and treatment objectives

Potable water treatment objectives are primarily focused on removing suspended material, oxidising dissolved organic and inorganic material, disinfection of a variety of pathogens, and ensuring stable and non-aggressive water. (The interested reader can also refer to the case studies in Chapter 8 for specific notes on how some of these challenges were addressed in practice.)

The challenges related to potable water *distribution systems* were also included and it should be noted that distribution system challenges require a different approach compared to water treatment challenges. The key reason for this is that strong oxidants applied post treatment in the distribution system can lead to the oxidation of organic and inorganic materials, which can result in the subsequent precipitation of a variety of insoluble material. Once the water reaches the distribution system it is very difficult to implement additional treatment processes except maybe for booster disinfection and point-of-use devices.

The typical challenges that can be expected at a potable water treatment works (WTW) and in potable water distribution systems are summarised below.

3.5.1.1 Colour

Colour is normally associated with the presence of humic and fulvic acids in the water. This can originate from decaying plant material (typically Cape water), algal activity or incomplete treatment of industrial effluent. Colour can also be present as a result of high metal content (iron, manganese and copper). Colour can be removed through oxidation, but the oxidant needs to be carefully selected in order not to create undesirable oxidation or DBPs. Other processes such as coagulation and phase separation can also be used for colour removal.

High levels of colour⁵ experienced in a distribution system needs to be investigated and preferably addressed at the source. In some cases it can be related to dirty distribution systems that may need flushing, corrosion of iron or copper based piping, or poor treatment at the source. Point-of-use devices can be used if only small areas of the distribution system are affected.

⁵ White water is linked to the presence of air bubbles. Yellowish or brownish water is often linked to the presence of iron. Bluish or greenish water is often linked to copper corrosion and can also be linked to the presence of algae (chlorophyll-a). Dark brown, black or even pinkish water is linked to the various oxidation states of manganese.

3.5.1.2 Taste and odour

Taste and odours are normally associated with the presence of dissolved volatile organics such as Geosmin and 2-Methyl Iso Borneol (MIB). These organic compounds can originate from algal and/or bacterial activity in impoundments, distribution systems or from pollutants in the wastewater, disposed into the catchment. Dealing with taste and odour compounds requires careful consideration of a number of aspects and is one of the most difficult challenges to deal with. Taste and odour compounds are oxidised by destructing the aromatic bonds. These compounds can also be adsorbed onto activated carbon. Knowledge about the nature of the odorous compound is essential in the identification of the source and consequent selection of an appropriate treatment process.

Taste and odour occurrences in a distribution system can be caused by a number of aspects such as bacterial re-growth, nitrification, sediment accumulation, anaerobic conditions in stagnant zones, and taste and odour production as by-products of the final disinfectant. The root cause(s) needs to be investigated and preferably addressed at the source. In some cases the taste and odour problems can be related to dirty distribution systems that may need flushing, booster disinfection or shock treatment with chlorine. Point-of-use devices with activated carbon filters can be considered if only small areas of the distribution system are continuously affected.

3.5.1.3 Dissolved iron

Dissolved iron is often experienced in impoundments and ground water sources. Iron is responsible for a brownish colour in the water. Iron can be effectively oxidised by a number of processes as described in Chapter 4. It is essential to provide for a phase removal step to remove the iron precipitate after oxidation. The effectiveness of iron oxidation (and reaction rate) is affected by a number of factors such as pH, temperature, organic complexation, chelation and a number of other inhibitor compounds including sulphates and silicates. The oxidation of iron and manganese is a complex process and needs to be supported by laboratory or pilot plant tests before a final process selection can be made.

The causes for high iron concentrations in a distribution system need to be investigated. If it is found that the root cause is not at the source, an appropriate distribution system operation and maintenance improvement plan needs to be put in place to address the increase in iron levels.

3.5.1.4 Dissolved manganese

Dissolved manganese is often experienced together with iron in impoundments and ground water sources. Manganese is responsible for a blackish or brownish colour in the water. Similar to iron, manganese can also be effectively oxidised by a number of processes, but it is essential to provide for one or more phase removal processes to remove the manganese precipitate after oxidation. The effectiveness of manganese oxidation is, similar to iron, affected by a number of factors. Manganese is often more difficult to oxidise and requires stronger oxidants, a higher reaction pH and longer reaction times.

Unlike iron, manganese is unlikely to be generated in the distribution system as steel pipes normally contain very little manganese. If manganese is identified in the distribution system it originated from the treatment works and is most probably re-suspended sediment that accumulated in a reservoir or a stagnant zone. Sudden flow changes and very low reservoir levels can result in a sudden release of the sediment.

High levels of manganese in the distribution system can be addressed by optimising the manganese removal at the WTW and through an appropriate distribution system operation and maintenance plan that includes regular flushing and cleaning of reservoirs and pipelines.

3.5.1.5 Turbidity

Turbidity requires a phase separation process and oxidation processes will generally not aid in the removal of suspended solids. However, in cases where dissolved metals are oxidised the precipitate that forms will be measured as turbidity.

Suspended iron and manganese in the distribution system are often measured as increased turbidity and can be a simple measure to monitor the condition of the distribution system.

3.5.1.6 Algae

The presence of algae cells requires a phase separation step such as sedimentation, dissolved air flotation, filtration or combinations of two or more processes for effective removal. Oxidants are often used to disable or disrupt algae cells before treatment. The oxidant will however not be able to remove the algal material. In some cases the algal cells will be ruptured which will require additional treatment in order to remove the algal metabolites or algal 'skeletons'. It should also be noted that the impact of an oxidant is dependent on the type of algae present. Some algae may only be affected in terms of their mobility while others may be completely ruptured and destroyed. Taste, odour and colour compounds may also develop as a result of oxidation of algal biomass.

Algae in a distribution system normally points towards poor treatment or a distribution system with reservoirs exposed to sunlight.

3.5.1.7 Chlorophyll-a

Elevated Chlorophyll-a concentrations are associated with the presence of algae and are quantified by measuring the green pigment (chlorophyll-a) of the algae. The green colour of chlorophyll-a can be oxidised with a number of oxidants, discussed in Chapter 4.

3.5.1.8 Dissolved organic carbon

Dissolved organic carbon originates from natural organic matter (NOM) in the dam or river system and presents a significant challenge to any water treatment plant. This is because the nature of the DOC needs to be known before an effective treatment process can be selected to remove it. A conventional DOC treatment train normally involves an oxidation step, a phase separation step and an activated carbon adsorption step.

The reaction between an oxidant and NOM or DOC compounds is highly dependent on the nature of the water and in particular, the nature of the organic compounds, the pH and temperature of the water, the oxidant type and the dosage applied. A considerable amount of data is required to select the appropriate combination of oxidants and disinfectants that are required to limit the formation of DBPs. The discovery that THMs and haloacetic acids (HAAs) are formed when using chlorine in the presence of certain types of DOC has sparked a plethora of studies to determine the by-products associated with different types of disinfectants. A list of the most common DBPs and the associated disinfectants is given in Table 3.

Table 3 – List of known DBPs (USEPA, 1999)

Group 1 – Inorganic by-products	Group 3 – Halogenated organic by-products Trihalomethanes (THMs)
Chlorate ion Chlorite ion Bromate ion Iodate ion Hydrogen peroxide Ammonia	Chloroform Bromodichloromethane (BDCM) Dibromochloromethane (DBCM) Bromoform Total trihalomethanes
Group 2 – Organic oxidation by-products	Haloacetic acids (HAAs)
Aldehydes	Monochloroacetic acid Dichloroacetic acid (DCA) Trichloroacetic acid (TCA) Monobromoacetic acid Dibromoacetic acid Total haloacetic acids
Formaldehyde Acetaldehyde	Haloacetonitriles
Chloroacetaldehyde	Chloroacetonitrile (CAN) Dichloroacetonitrile (DCAN) Trichloroacetonitrile (TCAN) Bromochloroacetonitrile (BCAN) Dibromoacetonitrile (DCAN) Total haloacetonitriles
Dichloroacetaldehyde	Haloketones
Trichloroacetaldehyde (chloral (chloralhydrate)	1,1-Dichloropropanone 1,1,1-Trichloropropanone Total haloketones
Glyoxal	Chlorophenols
Hexanal	2-Chlorophenol
Heptanal	2,4-Dichlorophenol
Carboxylic acids	2,4,6-Trichlorophenol
Hexanoic acid	Chloropicrin
Heptanoic acid	Chloral hydrate
Oxalic acid	Cyanogen chloride
Assimilable organic carbon	N-organochloramines
Nitrosoamines	MX (3-chloro-4 dichloromethyl 5 Hydroxy-2(5H)-furanone)
N-nitrosodimethylamine (NDMA)	

3.5.1.9 Bacteria and viruses

Bacteria and viruses occur in the different raw water sources and can be effectively treated with a range of disinfectants. The removal efficiency is often expressed in orders of magnitude or log removal. Different log removals can be achieved depending on the disinfectant used. The effectiveness of the different disinfectants is discussed in Chapter 4.

Water leaving a WTW should be bacteria and virus free after final disinfection. High bacteria counts in the distribution system are therefore mostly associated with poor disinfection during treatment, a loss of disinfectant residual and/or introduction of dirt during pipe bursts, poorly sealed reservoirs, etc. The loss of residual disinfection is discussed in more detail later in this section. The cause of the high

bacteria counts needs to be established and preferably addressed at the source and by implementing appropriate distribution system operation and maintenance practices.

3.5.1.10 *Cryptosporidium*

Cryptosporidium spp. cannot generally be treated effectively with conventional water treatment processes. If a *Cryptosporidium* sp. is present in the catchment, special disinfection strategies are required to inactivate these oocysts due to their extreme resistance to chlorine. Specific guidelines have been developed to ensure effective treatment using stronger disinfectants such as ozone, chlorine dioxide and UV radiation. Disinfection effectiveness is influenced by aspects such as pH, temperature, disinfectant type, disinfectant dose, contact time and disinfectant demand from substances other than the target organisms.

The presence of *Cryptosporidium* or *Giardia* in the distribution system, if not present immediately after treatment, indicates a contaminated distribution system.

3.5.1.11 *Giardia*

Giardia spp. present similar challenges to *Cryptosporidium*, albeit not as stringent, as *Giardia* is less resistant to chlorine. Effective treatment of *Giardia* can be performed by chlorine, but it is often more cost effective to use a stronger disinfectant such as ozone, chlorine dioxide or UV radiation.

3.5.1.12 Cyanobacterial toxins

Cyanobacterial toxins are linked to the presence of blue-green bacteria, namely Cyanobacteria, and can in some cases not be removed with conventional treatment processes. Algal toxins can either be oxidised with a strong oxidant such as ozone or adsorbed onto activated carbon, or in some cases a combination of ozonation and activated carbon. A range of algal toxins is known and the appropriate treatment process depends on the type of toxin and the concentration thereof (Newcombe, 2002).

3.5.1.13 Ammonia

A conventional WTW is not designed to remove high concentrations of ammonia. Ammonia presents a significant challenge to a conventional WTW and originates from semi- or untreated effluent or decaying organic material. Ammonia treatment can be achieved in a number of ways. Chemical treatment involves the oxidation of ammonia using chlorine. Very high levels of free ammonia will require excessive amounts of chlorine which will present other water treatment challenges such as the formation of DBPs. Ammonia at elevated levels is more effectively removed with biological pre-treatment processes referred to as nitrification and de-nitrification. The nitrification process converts ammonia to nitrate and nitrite, and the de-nitrification process converts the nitrate to nitrogen gas.

If the ammonia originates from a treated sewage source the raw water may also contain elevated levels of other nutrients such as ortho-phosphate, nitrate and DOC. Failure to address these elevated nutrient levels at the source or during treatment will impact on subsequent filtration and disinfection systems.

It should be noted that organo-chloramines are formed in the presence of organic nitrogen instead of monochloramines. The organo-chloramines do not have the same disinfecting qualities as monochloramines formed with inorganic ammonia and will render the disinfection process ineffective (Degrémont Suez, 2007).

High ammonia in distribution systems is often found where chloramine is used and is as a result of the decay of the chloramine or the improper control of ammonia dosing during the chloramination process. The reason for the chlorine decay needs to be established and be addressed either at the treatment plant, the point at which the ammonia is formed, or in the distribution system where the decay of the chloramines occurs.

3.5.1.14 Chemical oxygen demand

Similar to ammonia, high chemical oxygen demand (COD) levels should not normally be experienced by a potable water treatment plant as this would be an indication of poorly treated sewage effluent or pollution from an untreated effluent source. The DWAF general standard limits the COD concentration to 60 mg/L. High COD in a raw water source will normally also be associated with high coliform counts, high levels of ammonia, DOC and phosphates. It would often be more effective to address the high COD at the source, i.e. the upgrade or improved operation of WWTW.

3.5.1.15 Low disinfectant residual

Low disinfectant can be experienced at the point of primary chlorination or in the distribution system. In both cases the reason for the chlorine decay needs to be investigated. Substances that often increase the chlorine demand include suspended material with a chlorine demand, DOC, iron, manganese, ammonia, nitrate and algae. The process design should ensure that most of the substances creating an excessive disinfectant demand be removed before chlorine disinfection is attempted. If this is not the case, chlorine decay will be experienced resulting in challenges in the distribution system.

Low disinfectant residual or rapid loss of residual disinfectant can also be caused by distribution system infiltration and challenges related to nitrification, re-growth of micro-organisms in the distribution system and iron oxidation of unprotected ferrous pipeline material.

3.5.1.16 Disinfection by-products

The formation of DBPs is generally associated with the use of chlorine in the presence of NOM. Alternative disinfectants, however, have also been found to produce DBPs as a result of either reactions between disinfectants and compounds in the water or as a natural decay product of the disinfectant itself (USEPA, 1999). The DBPs can be grouped into three categories and a list of known DBPs, arranged by group, is given in Table 3 (p. 19).

- Halogenated organics, such as THMs, HAAs, halo ketones, and others, that are produced primarily as a result of chlorination.
- Organic oxidation by-products such as aldehydes, ketones, assimilable organic carbon (AOC), and biodegradable organic carbon (BDOC), that are associated primarily with strong oxidants such as ozone, chlorine, and advanced oxidation.
- Inorganics such as chlorate and chlorite, associated with chlorine dioxide, and bromate, which is associated with ozone, and has also been found when chlorine dioxide is exposed to sunlight.

The USEPA has also developed a list that indicates the implications of using a particular disinfectant. The slightly adapted version is indicated in Table 4.

Table 4 – Typical disinfectant properties (USEPA, 1999)

Condition	Chlorine	Ozone	Chlorine dioxide	Permanganate	Chloramine	Ozone / peroxide	Ultraviolet
Produce THM with TOC	y	s	n	n	y	s	n
Produce oxidised organics	s	y	s	s	n	y	s
Produce halogenated organics	y	s	n	n	y	s	n
Produce inorganic by-products	n	s	y	n	n	s	n
Lime softening impacts	y	n	n	n	y	n	y
Turbidity impacts	n	s	n	n	n	s	y
Meet <i>Giardia</i> - <2.0 log	y	y	y	n	n	n	n
Meet <i>Giardia</i> - >2.0 log	n	y	y	n	n	n	n
Meet <i>Cryptosporidium</i> - <2.0 log	n	y	y	n	n	n	n
Meet <i>Cryptosporidium</i> - >2.0 log	n	y	n	n	n	n	n
Meet virus - <2.0 log	y	y	y	n	n	n	y
Meet virus - >2.0 log	y	y	y	n	n	n	y
Secondary disinfectant	y	n	s	n	y	n	n
Operator skill (1=low; 5=high)	1	5	5	1	2	5	3
Applicable to large utilities	y	y	y	y	y	y	n
Applicable to small utilities	y	y	y	y	y	y	y

y = yes, n = no, s = sometimes

As mentioned earlier, the type and amount of DBPs produced during a treatment process depends largely on disinfectant type, water quality, treatment sequences, contact time, temperature and pH.

Disinfection by-products can be formed in the WTW as well as the distribution system. It should be noted that a fine balance needs to be struck between ensuring sufficient disinfectant residual for proper inactivation of pathogens and limiting the disinfectant dose to limit the formation of DBPs.

3.5.2 Disinfection guidelines

3.5.2.1 General disinfection guidelines

Disinfection of an organism requires knowledge of the organism, the type of disinfectants that can be used to inactivate the organism, the time the organism needs to be exposed to the disinfectant and the disinfectant concentration required to achieve a 'kill'.

Once the target organism(s) has been identified and appropriate disinfectants have been selected only two parameters remain to be selected; the disinfectant dose and contact time. A process parameter used in assessing the disinfection efficiency is the product of disinfectant concentration (C) and the effective disinfectant contact time (T) product, or commonly referred to as the CT value.

It is worth noting that the level of disinfection is not only determined by the disinfectant concentration and contact time, but also the reaction temperature and pH.

This has over many years lead to the development of CT guidelines which indicates the minimum required disinfectant concentration and contact time for a specific pH and temperature. Some guidelines also include the level of inactivation in terms of log removal. Typical CT requirements for different target organisms, expressed in mg/L.min and log removals are included in Chapter 4.

It is important to note that each CT requirement also states the log removal that is applicable to the specific CT requirement. High log removal rates will require higher levels of disinfection and higher CT values.

Once the concentrations of the specific pathogens are known in the raw water source, the required CT values can be determined for the selected disinfectant. Once this is known, the disinfection dosing rate and contact tank size can be determined to provide the required CT value.

3.5.2.2 Establishing effective contact time

The selection of the effective contact time is a subject that may appear simple on the surface, but needs to be approached with great care. A number of cases exist where contact tanks were provided to achieve a specific theoretical retention time only to find after construction that the actual retention time was only a fraction of the required contact time. The only corrective measure in such a case is to increase the disinfectant dose. Not only does this add to an increase in the ongoing operational cost, but can also result in the formation of DBPs.

Numerous case studies have been performed to determine the effective contact time of clear water contact tanks and storage reservoirs in South Africa using Computational Fluid Dynamics (CFD), a tool that enables the user to simulate the hydrodynamic behaviour of a process tank. Linked with special mathematical models, CFD can also be used to simulate the inactivation of a particular organism. This tool is bound to become a standard contact tank design tool (van der Walt, 2002).

3.5.3 Oxidation guidelines

Oxidation guidelines are water specific and cannot be generalised as is the case for disinfection. Oxidation requirements depend not only on the target matter that needs to be oxidised, but also the background substances and materials that inhibit the oxidation process.

The literature reports oxidation rates and requirements for oxidation reactions in synthetically prepared stock solutions that do not contain inhibitor substances. In reality this is seldom the case and oxidation reactions are often much slower due to the interference of the inhibitor substances.

Some of the typical oxidation reactions reported include the oxidation of iron and manganese using oxidants such as oxygen, chlorine, potassium permanganate and ozone. References such as Faust and Aly (1998) should be consulted for a comprehensive description of iron and manganese oxidation rates for different oxidants.

The oxidation of organic compounds is even more complicated, especially if the water originates from a polluted source. Laboratory and pilot scale studies are required to identify the oxidation reactions, reaction speed and products that are formed. In some cases undesirable organocomplexes and DBPs can be formed that can present health concerns.

3.5.4 Municipal and industrial wastewater treatment challenges and treatment objectives

3.5.4.1 General approach

The primary objective of a wastewater treatment plant is to remove carbon, nitrogen (in its various forms) and phosphates from the effluent. The effluent also needs to be disinfected. Municipal wastewater works employ biological processes for the treatment of effluent. Biofiltration and activated sludge treatment processes are the most common treatment processes employed. In some cases, where very low phosphate removal is required, chemical treatment is also employed as a polishing step. Disinfection is only applied at the end of the treatment process. In South Africa, disinfection of treated effluent is currently often performed using different forms of chlorine or in the exceptional case with ozone or UV. The disinfection effectiveness is affected by a number of substances as discussed in the previous section. Due consideration should be given to all the factors when selecting an appropriate disinfectant.

It should, however, be noted that the South African effluent guidelines do not currently require minimum effluent standards for different pathogens apart from coliform bacteria. Application of the water treatment disinfection guidelines to wastewater effluent will therefore result in demanding disinfection requirements. The subject of effluent standards and disinfection of municipal wastewater effluent will require additional regulation in view of the increased re-use of water.

The municipal wastewater treatment challenges that were included in sections 3.5.1.2 to 3.5.1.5 are based on the requirements of the current South African effluent guidelines (in countries such as the United States additional requirements are imposed on effluent discharge, especially if the effluent is intended for re-use).

Treatment challenges for industrial water treatment are very site specific and diverse, and depend on the type of industry, raw products, reagents, waste streams and products. Although such a diverse range of challenges falls beyond the scope of this text, three of the most common challenges were included in sections 3.5.1.6 to 3.5.1.8.

3.5.4.2 Chemical oxygen demand

Chemical oxygen demand is a measure of the substances in the effluent that can be oxidised. Most wastewater treatment plants employ some form of biological treatment process to reduce COD levels. The most commonly used wastewater treatment processes employed in South Africa include pond systems, biofilters and activated sludge processes.

It is not recommended to use chemical oxidants to treat high levels of COD for the reasons previously mentioned.

3.5.4.3 Nitrogen (ammonia and nitrate)

Nitrogen in the form of ammonia, nitrate and/or nitrite is found in municipal effluent and is also treated in biological wastewater treatment plants. Ammonia is removed by a biological process referred to as nitrification. Oxygen is dissolved into the effluent as an 'oxidant' to enable nitrifying bacteria to convert ammonia into nitrates. Using a series of recycle streams most of the nitrified ammonia is recycled back to an upstream process where nitrates, in the absence of oxygen, are converted by de-nitrifying bacteria to nitrogen gas.

It is impractical to attempt nitrogen removal in any form using non-biological treatment processes. Unfortunately, if the nitrogen levels leaving a wastewater treatment are not below the regulated concentrations, WTW are often forced to practice chemical oxidation or experience distribution system quality problems due to post-treatment nitrification.

3.5.4.4 Phosphates

Phosphates can be removed from water by precipitating the phosphates using ferric chloride or lime. This is often only applied as a polishing step or as an emergency measure. Some wastewater treatment plants are designed to achieve biological removal of phosphates. Phosphates at elevated levels in the effluent discharged into a river system or dam can lead to excessive algal growth and should be prevented as this will lead to expensive upgrades required on downstream WTW. Phosphates are also used in some industries as a corrosion inhibitor or sequestering agent and will delay the oxidation of iron. Oxidants are not effective in dealing with phosphates.

3.5.4.5 Faecal coliforms

In order to reduce the high faecal coliform counts of final effluent before it is discharged into the river system a disinfectant is used. In South Africa, the most common disinfectant used at WWTW is chlorine. In some cases UV radiation has been applied with limited success. There are currently no systematic results available of the level of disinfection that is achieved for any other pathogen apart from faecal coliform indicator organisms. There are also no systematic data on the CT requirements for wastewater effluent disinfection. Using chlorine may therefore reduce the faecal coliform levels within the legal requirement, but other pathogens may still be active.

In view of this, it is recommended that the final effluent be screened to identify and enumerate the pathogens present if the water discharged from a WWTW is intended for direct or even indirect re-use. Using this approach will not only guide the disinfection required at the WWTW, but also the treatment process required at the downstream water works.

3.5.4.6 Metal content

High metal content is one of the most common challenges found at mining and industrial WTW. High metal content can be removed in a number of ways and often involves the oxidation of the metal salt into an insoluble form which then forms a precipitate that can be removed by means of sedimentation, flotation or filtration phase separation processes. Metals that are responsible for hardness such as calcium and magnesium can be removed by softening processes.

Oxidation of iron and manganese using different processes are discussed in Chapters 4 and 5. It should be noted that the oxidation reaction speed is determined to a large extent by the reaction pH, temperature and other inhibitor compounds. References such as Faust and Aly (1998) provide oxidation rates for various metal and oxidant combinations.

The high lime process presents a unique scenario where lime in the form of Ca(OH)_2 is added to increase the pH. This achieves several objectives. The lime acts as a coagulant and seeding agent for flocculation, it increases the pH which will assist with the precipitation of manganese, and finally the combination of the high lime and elevated pH also has a disinfection effect. Subsequent to sedimentation the pH needs to be reduced using CO_2 . This process has been practised by Rand Water for many years with great success.

A study conducted in the US demonstrated significant reduction in coliform levels after high lime treatment (Conway *et al.*, 2008).

Other examples exist where the addition of a metal salt (e.g. ferric chloride) can assist in the removal of a metal in an undesirable oxidation state (e.g. chrome(VI), hexavalent chrome).

3.5.4.7 Dissolved solids

High dissolved solids or high salinity is a very common industrial water treatment challenge. Unfortunately, oxidants are generally not effective in removing salinity unless the salinity is associated with a metal salt which can be precipitated after oxidation.

3.5.4.8 Acidity

High acidity is often encountered where acid is used to adjust reaction pH. The control of acid mine water and its treatment is currently receiving a lot of attention in South Africa. The reader is referred to the *Best Practice Guidelines* prepared by DWAF (2008) for more in-depth information in this regard.

3.5.4.9 Scaling and fouling

Scaling and fouling are often encountered in cooling water circuits. Scaling and fouling of heat exchangers lead to slow heat transfer to cooling fluid and also high water losses as cooling circuits need to be flushed and replenished with fresh cooling liquid, or at the very least some cooling fluid needs to be removed and diluted with fresh cooling fluid. The fouling often occurs as a result of biological growth in the cooling circuits. Disinfection and oxidation of the cooling water can improve the efficiency of the heat exchangers by preventing the re-growth and removing some of the biofilm inside the heat exchanger and recycle pipe work.

3.6 INTRODUCTION TO THE SELECTION CHART

The process selection chart (Table 5) is a provisional guide to ascertaining which type of oxidation and disinfection process is indicated for the treatment challenges and objectives discussed in the previous paragraphs. The chart should be applied keeping in mind the limitations and requirements imposed by other non-oxidation and non-disinfection related treatment objectives and processes of the treatment train. An integrated process design exercise needs to be conducted following a provisional oxidation and disinfection process selection.

The chart consists of a number of rows listing the different types of oxidants and disinfectants and columns listing the typical oxidation and disinfection treatment challenges.

3.6.1 Description of selection chart columns

Column 1 distinguishes between *direct* disinfection processes through the addition of a chemical, radiation or heat source and an *indirect* disinfection process which occurs as a result of a phase separating process. Column 2 groups the processes into halogen types, metal ion types, ultraviolet types, oxygen based types, heat types, phase separating types and dissolved solid types. Column 3 lists each of the individual oxidation and disinfection processes. Column 4 provides the chemical formula for the active ingredient of the process (where available). Column 5 lists the reference paragraph in Chapter 4 where a detailed description of the process can be found. Columns 6 onwards list the water treatment challenges discussed for the different treatment works and were divided into a potable water treatment section, a potable water distribution system section, and a wastewater and industrial water treatment section.

3.6.2 Description of selection chart rows

Row 1 describes the industry type and Row 2 describes the most common water treatment challenges applicable to the specific industry. Row 3 lists the corresponding reference paragraph in Chapter 3.

3.6.3 Using the selection chart

The user can now use the chart in two ways. If the treatment challenge or objective is known, the user can select the appropriate column from Column 6 onwards and then assess the colour coding applicable to each process. The colour coding indicates the appropriateness of a particular treatment process for the selected treatment challenge.

- Process not recommended 
- Not commonly used, but possible 
- Average 
- Good 
- Ideal and commonly used 

In some cases a number was placed inside the coloured box with a note explaining the qualification placed on the specific process. As an example the chart indicates the following direct oxidation processes for a high manganese treatment challenge in order of preference:

- Ideal - Chlorine dioxide, ozone and potassium permanganate
- Good - Chlorine based oxidants
- Average
(depending on pH) - Oxygen/Air

Indirect processes that are recommended with the direct oxidation process include a number of phase separation processes such as sedimentation, filtration and dissolved air flotation.

Table 5 – Oxidation and disinfection process appropriateness selection chart

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37		
							Water												Municipal and Industrial Wastewater Treatment																				
							Treatment												Distribution																				
							High Colour	High Taste & Odour	High Iron	High Manganese	High Turbidity	High Algae	High Chlorophyll-a	High DOC	High Bacteria and virus	High Cryptosporidium	High Giardia	High cyanobacterial toxins	High Ammonia	High COD	Low Residual chlorine	High DBP	High Colour	High Taste & Odour	High Iron	High Manganese	High Bacteria and virus	High Ammonia	Low Residual chlorine	High COD	High Nitrogen	High Phosphates	High Faecal Coliforms	Scaling and fouling	High metal content	High dissolved solids	High acidity		
							3.5.1.1	4.5.1.2	3.5.1.3	3.5.1.4	3.5.1.5	3.5.1.6	3.5.1.7	3.5.1.8	3.5.1.9	3.5.1.10	3.5.1.11	3.5.1.12	3.5.1.13	3.5.1.14	3.5.1.15	3.5.1.17	3.5.1.11	3.5.1.12	3.5.1.13	3.5.1.14	3.5.1.19	3.5.1.13	3.5.1.15	3.5.1.2	3.5.1.3	3.5.1.4	3.5.1.14	3.5.1.13	3.5.1.15	3.5.1.9	3.5.1.6	3.5.1.7	3.5.1.8
							Chapter reference																																
1																																							
2																																							
3																																							
4							4.4																																
5							4.4	Chlorine gas																															
6							4.5	Chloramination																															
7							4.6	Chlorine dioxide																															
8							4.4	Sodium Hypochloride																															
9							4.4	Calcium Chloride (HTH)																															
10								Bromine																															
11								Iodine																															
12							4.1	Potassium Permanganate																															
13							4.11	Copper Ions																															
14							4.12	Silver Ions																															
15							4.13	High lime																															
16							4.14	Ultraviolet																															
17							4.8	Oxygen/Air																															
18							4.9	Ozone																															
19							4.16	Peroxone																															
20							4.15	O ₃ +H ₂ O ₂																															
21								UV and ozone																															
22								Water boiling																															
23								Sedimentation/Clarification																															
24								Filtration																															
25								Filtration: Rapid Sand																															
26								Filtration: Slow Sand																															
27								Filtration: GAC																															
28								Microfiltration																															
29								Ultrafiltration																															
								Nanofiltration																															
								Reverse Osmosis																															

Notes

- 1 Practical only on at point of use in cases of emergency
- 2 Not recommended to oxidise in distribution system as this will result in colour complaints.
- 3 Better addressed during treatment.
- 4 Better addressed during treatment.
- 5 Does not leave a residual and may oxidise dissolved iron and manganese which can lead to colour problems. Should rather be addressed during treatment.
- 6 Only effective as part of nitrification filters and/or aeration process
- 7 Not recommended requires additional phase separation step. Better performed during treatment.
- 8 A secondary benefit when enmeshed in lime flocs

Ideal
 Good
 Average
 Not common
 Not recommended/not effective

CHAPTER 4 – OXIDATION AND DISINFECTION PROCESSES

- 4.1 - Introduction
- 4.2 - Historical development of oxidation and disinfection processes
- 4.3 - Oxidation and disinfection process fundamentals and selection criteria
- 4.4 - Chlorine
- 4.5 - Chloramination
- 4.6 - Chlorine Dioxide
- 4.7 - Ozone
- 4.8 - Ultraviolet radiation
- 4.9 - Potassium permanganate
- 4.10 - Copper and silver
- 4.11 - Advanced oxidation processes (AOP)
- 4.12 - Alternative disinfection processes
- 4.13 - Secondary disinfection processes

4.1 INTRODUCTION

This section describes the typical oxidation and disinfection processes found in industry, the manner in which the processes are normally applied and some fundamental concepts regarding the processes.

Chemical oxidants are used in water treatment processes for the oxidation of compounds such as reduced inorganic species, e.g. ferrous iron (Fe(II)), manganous manganese (Mn(II)) and sulphides as well as hazardous synthetic organic compounds such as atrazine. A further important application in potable water treatment is the removal of taste and odour compounds such as geosmin and MIB. It has also been reported in some cases that they may improve the performance of, or reduce the required amount of coagulants. Because many oxidants also have biocidal properties they can be used to control nuisance aquatic growths such as algae and are also used as primary disinfectants to meet CT (disinfectant concentration x contact time) required for a specific pathogen. These oxidants are often added to the raw water at the head of the works, but they can also be employed after clarification after a substantial portion of the oxidant demand has been removed (MWH, 2005).

The most common chemical oxidants used in water treatment are chlorine, chlorine dioxide, ozone and permanganate. Ozone is sometimes used in conjunction with hydrogen peroxide or ultraviolet irradiation to produce radicals that have powerful oxidative properties. Due to the dual purpose of these chemicals (oxidation and disinfection), the designer must be aware of the purpose of employing a certain technology. The use of ozone, for example, is an excellent oxidant for the oxidation of iron and manganese, while it can also be employed for disinfection of harmful pathogens. The disadvantage of ozone, however, is that the decay is quite rapid and this is the reason why chlorine is preferred for secondary disinfection (in the distribution system) requirements. Should the distribution system be such that a very long contact period occurs (> 10 days), even chlorine will decay and then provision must be made for either intermittent chlorination, or a disinfectant such as mono-chloramination can be used.

With the concern for the removal and inactivation of pathogens such as *Giardia* and *Cryptosporidium*, while minimising DBPs, options other than traditional chlorination are gaining popularity. The addition of chlorine is then often extended and only added after the bulk of the organic material has been removed. The purpose of this section is to provide an introduction to the major type of oxidants and disinfectants available and to provide some guidelines on which technology to utilise for certain applications.

The purpose of this section is to provide an introduction to the major type of oxidants and disinfectants available and to provide some guidelines on which technology to utilise for certain applications.

4.2 HISTORICAL DEVELOPMENT OF OXIDATION AND DISINFECTION PROCESSES

4.2.1 Chlorine

Chlorine gas was first prepared in 1774, but chlorine was not regarded as a chemical element until 1808 (AWWA, 1999). Disinfection of water by chlorine first occurred in 1908 at Bubbly Creek (Chicago, USA) and at the Jersey City Water Company. It was found that a dramatic reduction in typhoid accompanied the introduction of this process and by 1918 over 1000 cities, treating more than 11 billion ML/d of water, were employing chlorine as disinfectant.

4.2.2 Chloramination

The addition of both chlorine and ammonia, either sequentially or simultaneously, was first employed in Ottawa, Canada and Denver, Colorado in 1917 (AwwaRF, 1991). The process was advocated for its ability to prolong the stability of residual disinfectant during distribution and for its diminished propensity to produce chlorophenolic taste and odour substances. Difficulties surrounding the dosing of ammonia (a certain Cl to NH₃ ratio is required), reduced the popularity of this process; however, recent advances in automation and accurate monitoring instrumentation partly resolved this problem.

4.2.3 Chlorine dioxide

Chlorine dioxide was first produced from the reaction of potassium chlorate and hydrochloric acid in 1811 (Miller *et al.*, 1978). Although widely used as a bleaching agent in pulp and paper manufacture, the use of this technology in both water and wastewater treatment has been slow. As recently as 1971, it was stated that "... ClO₂ has never been used extensively for water disinfection". By 1977, 84 potable water treatment plants in the USA were identified as using chlorine dioxide treatment. In Europe, chlorine dioxide was being used as either an oxidant or disinfectant in almost 500 potable water treatment plants (Miller *et al.*, 1978).

4.2.4 Ozone

This molecule was discovered in 1783 by Van Marum and named by Schonbein in 1840. In 1857, the first electric discharge ozone generation device was constructed by Siemens, with the first commercial application of this device occurring in 1893 (Rakness *et al.*, 1984). Ozone was first applied as a potable water disinfectant in 1893 at Oudshoorn, Netherlands. In 1906, Nice, France installed ozone as a treatment process (Rice *et al.*, 1978) In the USA, ozone was first employed for taste and odour control at New York City's Jerome Park Reservoir in 1906. In 1987, five water treatment facilities in the USA were using ozone primarily for taste and odour control or THM precursor removal (Glaze, 1987). Since the 1993 Milwaukee *Cryptosporidium* outbreak, there has been an upsurge in interest in ozone as a disinfectant.

4.2.5 Ultraviolet (UV) irradiation

The biocidal effects of UV radiation have been known since it was established that short wavelength UV was responsible for microbial decay often associated with sunlight (Block, 1991). By the early 1940s design guidelines for UV disinfection were proposed. UV has been accepted for treating

potable water on passenger ships; however, it has been met with little enthusiasm in public water supply applications because of the lack of a residual following application. In wastewater treatment, in contrast, over 600 plants in the USA were using UV disinfection facilities by 1991 (Block, 1991).

4.2.6 Potassium permanganate

In 1659 a German chemist, J.R. Glauber, fused a mixture of the mineral pyrolusite and potassium carbonate to obtain a material that, when dissolved in water, gave a green solution (potassium manganate) which slowly shifted to violet potassium permanganate, and then finally red (USEPA, 1999). Only in 1800 did it become a common household and institutional disinfectant. It was first used for water treatment in 1910 in London but did not begin to grow in use until the 1960s, when applications for taste/odour control were publicised. According to a survey by the AWWA research foundation for plants serving more than 10 000 people, 36.8% of these plants use this chemical for pre-treatment, pre-oxidation and organics removal (USEPA, 1999).

4.3 OXIDATION AND DISINFECTION PROCESS FUNDAMENTALS AND SELECTION CRITERIA

The selection of a specific oxidant and/or disinfectant hinges on a number of aspects such as the effectiveness of the specific process for a specific application, the impact and benefits or other processes in the treatment train, the cost associated with its use and the supportability of the process. A distinction needs to be made between the capital and operating cost. The combination of the two cost aspects indicates the life cycle cost and can assist in selecting the most cost effective technology.

The chapters below describe in detail the typical oxidation and disinfection processes found in the industry, the manner in which the processes are normally applied and some fundamental concepts regarding the processes. In each chapter, a section on selection criteria for the common problems found in the various industries is provided, which link to the discussion on the selection chart as described in Chapter 3.

- Basic chemistry.
- Oxidant demand.
- Disinfectant demand.
- Disinfectant by-products.
- Selection criteria.
- Contact time and verification.
- Costs.

The oxidation and disinfection processes discussed below have been grouped into chlorine based processes, oxygen based processes, metal based processes, irradiation processes, advanced processes, alternative disinfectants and other indirect processes.

The chlorine based processes include the following:

- Chlorine (gas and hypochlorite variants)
- Chloramines
- Chlorine dioxide

The oxygen based processes include ozone.

The metal based processes include:

- Potassium
- Copper
- Silver
- Calcium

Irradiation processes include UV radiation.

Alternative disinfection processes include:

- Heat
- Bromine
- Iodine

Advanced oxidation processes include:

- Peroxide/ultraviolet light ($\text{H}_2\text{O}_2/\text{UV}$)
- Ozone/ultraviolet light (O_3/UV)
- Hydrogen peroxide/ozone ($\text{H}_2\text{O}_2/\text{O}_3$)
- Hydrogen peroxide/ozone/ultraviolet ($\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$)
- Fenton's reagent with ozone and/or UV

4.4 CHLORINE

4.4.1 Basic chemistry

Chlorine may be used in the form of compressed gas under pressure that is dissolved in water at the point of application, solutions of sodium hypochlorite, or solid calcium hypochlorite. The relative amount of chlorine present in chlorine gas, or in the other forms, is expressed in terms of available chlorine. Chlorine gas hydrolyses rapidly in water to form hypochlorous acid (HOCl). The following equation presents the hydrolysis reaction (USEPA, 1999):



Note that the addition of chlorine gas to water reduces the pH of the water due to the production of the hydrogen ion. Hydrochlorous acid is a weak acid which means that it dissociates slightly into hydrogen and hypochlorite ions as indicated below:



Between a pH of 6.5 and 8.5 this dissociation is incomplete and both HOCl and OCl⁻ species are present to some extent. Below a pH of 6.5, no dissociation of HOCl occurs, while above a pH of 8.5, complete dissociation of OCl⁻ occurs. As the germicidal effect of HOCl is much higher than OCl⁻, chlorination at a lower pH is preferred.

Sodium hypochlorite solution typically contains 12.5% available chlorine and the reaction between sodium hypochlorite and water is shown as (USEPA, 1999):



It is seen that hypochlorous species is also produced. However, unlike chlorine gas hydrolysis, a hydroxyl ion is produced which will increase the pH of the water.

Calcium hypochlorite is a granular substance and contains approximately 65-70% available chlorine. The reaction between calcium hypochlorite and water is as follows (USEPA, 1999):



Hypochlorous acid is produced which is the preferred substance, and it is seen that the pH will also increase due to the production of the hydroxyl ion.

4.4.2 Oxidant demand

The presence of organic and inorganic substances in the water exerts an oxidant demand and the main consumers of free chlorine are:

Nitrogen: Nitrogen reacts with free chlorine in the water to form chloramines. The various reactions to form the various species of amines are described in section 4.5. As per the breakpoint graph indicated in Figure 1, it is seen that approximately 7.6 mg Cl₂ is required for every mg of ammonia (measured as N) in the water. In the case where the final product water from a treatment plant contains fairly high levels of ammonia, this constituent will exert a sizable chlorine demand which will affect operational costs (USEPA, 1999).

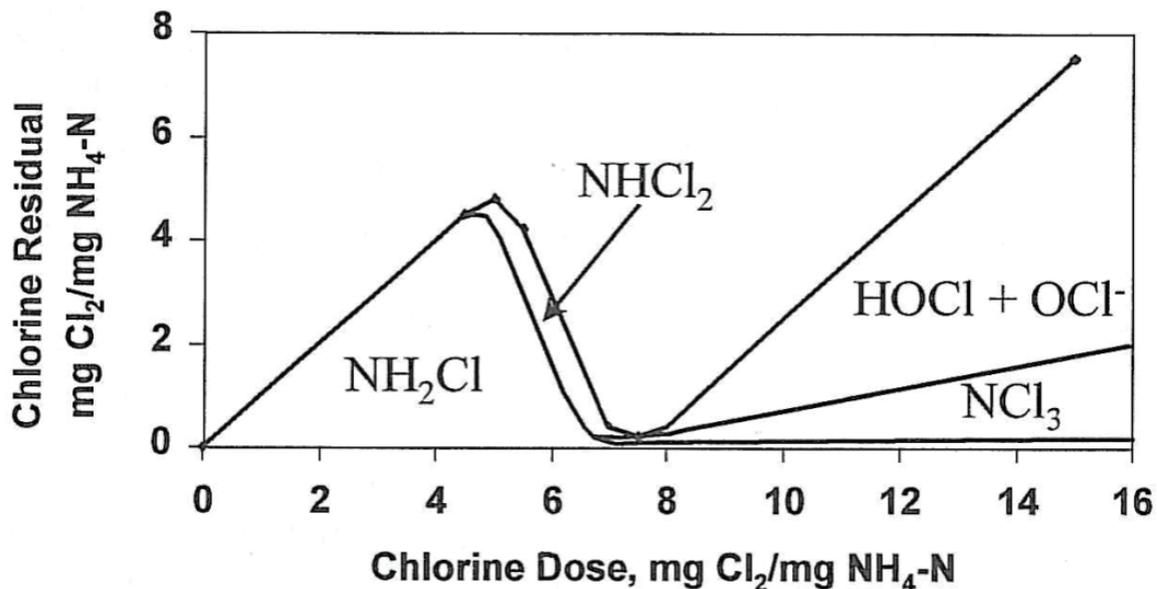


Figure 1 – Breakpoint chlorination curve (USEPA, 1999)

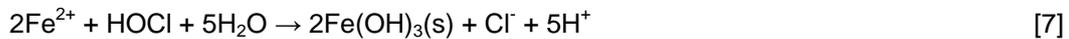
Sulphides: Under alkaline conditions, sulphide reacts rapidly with chlorine as follows:



By the first reaction, 2.1 mg Cl₂ is required per mg H₂S removed (at pH values >8). As the pH decreases, the chlorine requirement increases to 8.4 mg Cl₂ per milligram of H₂S removed (second equation).

Organic matter: The presence of organic material in the water is often measured as DOC, total organic carbon (TOC), UV absorbance at a wavelength of 254 nm or even COD – although the latter measurement also contains some chemical demands for inorganic elements. The reactions of chlorine with organic material are numerous and the formation of halogenated compounds, such as chloroform and bromoform are some of the well-known by-products formed.

Iron : Ferrous ($^{2+}$) iron is converted to ferric ($^{3+}$) iron by the following reaction with chlorine:



This reaction is quite rapid and generally completed in less than 15 minutes, even at low pH. The oxidation of ferrous iron is accelerated by high pH conditions and can be decelerated substantially by the presence of high levels of organic matter. The required chlorine dose for the oxidation of iron is about 0.63 mg $\text{Cl}_2/\text{mg Fe}^{2+}$.

Manganese: The oxidation of dissolved manganese, Mn(II) with free chlorine is more difficult than the oxidation of Fe(II). The reaction between chlorine and Mn(II) is too slow to be useful in water treatment unless the pH is >9. When chlorinated water is passed through a filter with media coated by MnO_2 , removal will occur by adsorption to the media and the adsorbed Mn(II) will gradually be oxidised to MnO_2 on the filter media surface.

The following reaction is applicable to the oxidation of dissolved manganese:



Approximately 1.29 mg chlorine per mg Mn^{2+} is required for oxidation and this reaction requires about 2 to 3 hours to be complete.

4.4.3 Disinfection demand

Chlorine is capable of producing lethal events at or near the cell membrane as well as affecting the DNA of a cell. Chlorine damages the cell wall membrane and promotes leakage through the cell membrane.

Bacteria inactivation: Chlorine is an extremely effective disinfectant for inactivating bacteria. Study results indicated that HOCl is more effective than OCl^- for inactivation of bacteria such as *Escherichia coli*, *Salmonella typhi* and *Shigella dysenteriae*. These results have been confirmed by several researchers that concluded that HOCl is 70 to 80 times more effective than OCl^- for inactivating bacteria (USEPA, 1999).

Virus inactivation: Chlorine has been shown to be a highly effective viricide. Tests performed to determine the resistance of 20 different enteric viruses to free chlorine under constant conditions of 0.5 mg/L free chlorine and a pH and temperature of 7.8 and 2°C respectively, indicated the least resistant virus to be rheovirus which required 2.7 minutes to achieve 99.99 percent inactivation (4 log removal). The most resistant virus was found to be a poliovirus, which required more than 60 minutes for 99.99 percent inactivation. The corresponding CT range required to achieve 99.99 percent inactivation for all 20 viruses was between 1.4 and over 30 mg.min/L (van der Walt, 1997).

Protozoa inactivation: Chlorine has been shown to have limited success when used for inactivating protozoa. Data obtained during a 1984 study indicated that the resistance of *Giardia* cysts are two orders of magnitude higher than that of enteroviruses and more than three orders of magnitude higher than the enteric bacteria (USEPA, 1999).

Chlorine also has little impact on the viability of *Cryptosporidium* oocysts when used at the relatively low doses encountered in water treatment (e.g. 5 mg/L). Studies indicated that “no practical inactivation was observed” when oocysts were exposed to free chlorine concentrations ranging from 5 to 80 mg/L at pH 8, a temperature of 22°C, and contact times of 48 to 245 minutes (Gyürék *et al.*, 1996). Concentration contact times ranging from 3 000 to 4 000 mg.min/L were required to achieve 1-log inactivation of *Cryptosporidium* at pH 6.0 and temperature of 22°C.

From the above studies, several so-called CT values (a function of log removal, temperature and pH) have been determined. The CT factor is defined as the product of the residual disinfectant concentration (C) in mg/L, and the contact time (T) in minutes, that the residual disinfectant is in contact with the water. Table 6 indicates the CT requirements for five different disinfectants for the inactivation of viruses (USEPA, 1999), while Table 7 shows comparable requirements for the inactivation of *Giardia* cysts.

Table 6 – Contact time values for inactivation of viruses (USEPA, 1999)

Disinfectant	Units	Inactivation		
		2-log	3-log	4-log
Chlorine ¹	mg.min/L	3	5	6
Chloramine ²	mg.min/L	643	1 067	1 491
Chlorine dioxide ³	mg.min/L	4.2	12.8	25.1
Ozone	mg.min/L	0.5	0.8	1
UV	mW.s/cm ²	21	36	Not available

¹ Values based on temperature of 10°C, pH 6 to 9 and free chlorine residual of 0.2-0.5 mg/L

² Values based on temperature of 10°C and pH of 8

³ Values based on temperature of 10°C and pH range of 6 to 9

Table 7– Contact time values for inactivation of *Giardia* cysts (USEPA, 1999)

Disinfectant	Inactivation (mg.min/L)					
	0.5-log	1-log	1.5-log	2-log	2.5-log	3-log
Chlorine ¹	17	35	52	69	87	104
Chloramine ²	310	615	930	1 230	1 540	1 850
Chlorine dioxide ³	4	7.7	12	15	19	23
Ozone	0.23	0.48	0.72	0.95	1.2	1.43

¹ Values based on temperature of 10°C, pH 7 and free chlorine residual of 0.4 mg/L or less

² Values based on temperature of 10°C and pH of 6 to 9

³ Values based on temperature of 10°C and pH range of 6 to 9

4.4.4 Disinfection and oxidation by-products

Halogenated organic by-products are formed when NOM reacts with free chlorine. The factors which affect the formation of these by-products include the type and concentration of NOM, the oxidant dose, time of contact, pH, organic nitrogen concentration and temperature. The DBPs formed include THMs, HAAs and cyanogen halides, which several laboratory studies have indicated to be carcinogenic (USEPA, 1999). Since the discovery of chlorination by-products, work has been conducted to try and prohibit the formation of these by-products and in general, the following five alternatives should be evaluated to reach this goal:

- Use an alternative disinfectant / oxidant
- Reduce the free-chlorine contact time
- Reduce the concentration of NOM before chlorine addition
- Remove bromide before chlorine addition
- Change the pH of the water during chlorination

4.4.5 Selection criteria (see selection chart)

For the typical water related problems as described in Chapter 3, the application of chlorine as an oxidant and disinfectant is as follows:

- i) High colour: High colour is normally associated with the presence of humic and fulvic acids in the water. Values up to 400 mg Pt/L in the Cape waters is not uncommon and the SANS 241 Class 1 limit for colour is 10 mg Pt/L. Chlorine is not commonly used for removal of colour due to the formation of DBPs, the ineffectiveness of chlorine for breaking the double bonds and the high dosages required.
- ii) Taste and odour: Where taste and odour are associated with geosmin and MIB, chlorine as an oxidant is not effective due to the resistance of the molecules to reaction. While chlorine dosing masks the effect of these tastes and odours, after time the chlorine will decay and the taste and odours will re-emerge. Chlorine is effective, however, in the removal of odours associated with reduced sulphur compounds.
- iii) High manganese: Dissolved manganese can be oxidised effectively by chlorine to the insoluble manganese dioxide (MnO_2) state; however, this reaction is more effective at elevated pH levels > 9.5. Stabilisation of the water will be required after oxidation.
- iv) High iron: The use of chlorine for the oxidation of dissolved iron to the insoluble ferric hydroxide ($Fe(OH)_3$) is effective and quick. Higher pH values (> 7.5) will be beneficial for the process.
- v) High turbidity: The removal of turbidity is a phase separation issue and chlorine addition will not aid in the removal of suspended solids. This technology is not effective if the aim is to remove turbidity.
- vi) High algae: Chlorine is effective in the rupturing of algal cells which can thereafter be removed by sedimentation and filtration.
- vii) High chlorophyll: The presence of algae in water is measured by measuring the green pigment in the algae (chlorophyll-a). As above, chlorine is effective in killing algae and will be able to bleach the chlorophyll afterwards – ‘bleaching’ the molecule, means that the chromophoric properties which give the chlorophyll the green colour are taken away by breaking (oxidising) the double bonds in the molecule.
- viii) High DOC: The reaction with organic compounds is highly dependent on the nature of the organic compound, other constituents in the water, pH and temperature. Some organic compounds are relatively easy to oxidise while others are more resistant. Additional to the above, the products of the reaction vary depending on the oxidant, the dosage and water quality characteristics. In general, chlorine is effective but not advisable in oxidising organic compounds; however, if utilised, it is preferable that the process occurs as late as possible to prevent excess THM formation.
- ix) High coliform: The effectiveness of chlorine in inactivating a broad range of bacteria and viruses is measured by the removal of the indicator organism coliform measured as total coliforms or faecal coliform. Chlorine is effective in obtaining a 3-4 log removal of coliforms.
- x) High Cryptosporidium: The *Cryptosporidium* oocyst is extremely resistant to chlorine as is reflected in no CT value being available for this pathogen – chlorine as a disinfectant is thus not recommended.
- xi) High Giardia: The CT value for inactivation of the *Giardia* cyst by 3 log removals is approximated by the following formula:

$$CT = 0.2828 \text{ pH}^{2.69} \text{ Cl}^{0.15} 0.933^{(1-5)} L$$

[9]

Where:

CT= Product of free chlorine residual and time required

pH = pH of water

Cl = Free chlorine residual, mg/L

T = Temperature, °C

L = Log removal

For a 3-log removal, 15 degrees temperature, 7 pH and a 2 mg/L residual a CT of 87 will be required. Conservatively, with a 2 mg/L residual, a contact time (T_{10}) of 43 minutes will be required. Chlorine is therefore effective for removal of *Giardia*.

- xii) High cyanobacteria toxins: Chlorination is a feasible option for microcystin degradation during oxidation and disinfection processes, and can be applied in drinking water treatment in case of cyanobacterial toxin risk if the pH is kept below 8.
- xiii) High ammonia: The amount of chlorine required to reach breakpoint, i.e. to oxidise all available ammonia, is about 7 mg/L chlorine per mg/L ammonia. For water with high free ammonia, the amount of chlorine to satisfy the demand only might be prohibitive and the use of chlorine for such an application is not recommended.
- xiv) High pathogen: As discussed under the pathogens, *Cryptosporidium* and *Giardia*, mixed success is obtained with using chlorine as a disinfectant. This application is specifically for an overall reduction in pathogens before treated waste water is discharged to a public water body.
- xv) High COD: As per South African standards, the levels of COD must be below a certain level before treated waste water can be discharged to public water bodies. Chlorine as an oxidant can oxidise organic compounds; however, the dosages will be very high should complete mineralisation (full oxidation to CO_2) be required. For the purpose of mineralisation, chlorine as an oxidant is not effective.

4.4.6 Environmental effects

Several environmental factors influence the inactivation efficiency of chlorine, including water temperature, pH, contact time, mixing, turbidity, interfering substances and the concentration of available chlorine. In general, the highest levels of pathogen inactivation are achieved with high chlorine residuals, long contact times, high water temperature and good mixing, combined with a low pH, low turbidity and the absence of interfering substances. Of the environmental factors, pH and temperature have the most impact on pathogen inactivation by chlorine.

As described earlier, the germicidal efficiency of hypochlorous acid (HOCl) is much higher than that of the hypochlorite ion (OCl^-), and since the latter species dominates at higher pH values, a low pH is preferred to increase the disinfection efficiency.

For typical drinking water temperatures, pathogen inactivation increases at higher temperatures. Virus studies indicate that the contact time should be increased by two to three times to achieve comparable inactivation levels when the water is lowered by 10°C.

4.4.7 Costs

Capital cost: The capital items required for a chlorine gas system include a room, normally divided into two areas – one for storage and the other as a dedicated dosing area. The storage area usually allows for storage of a month's supply and the chlorine cylinders are often stored on scales which

convey the amount of chlorine to a centralised SCADA (Supervisory Control and Data Acquisition) system. In the dosing room, the chlorinators are installed where the chlorine is injected into a service water stream by means of a venturi. If service water with pressures exceeding 400 kPa is not available on site, use is made of a separate booster pump to create these pressures required for injection of the chlorine. The chlorine enriched service water is then conveyed to the point of application where the physical dosing occurs. Mechanical / electrical cost items include the chlorinators, booster pumps, automatic switch over devices, scales, crane beam trolley, safety equipment, safety shower and free chlorine meter with associated PLC. Figure 2 indicates typical costs as a function of the kg Cl₂ required per hour (2009 costs).

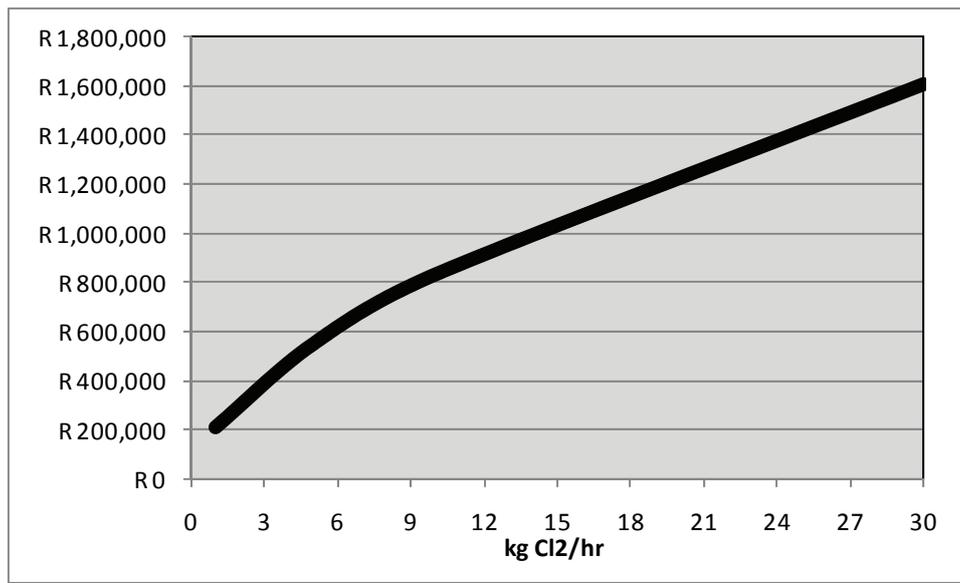


Figure 2 – Chlorination capital cost

Operational cost: The operational cost components consist of supply and delivery of the chemical, personnel cost, maintenance, electricity cost for the operation of the unit and capital redemption. For the sake of this manual, a typical calculation for calculating the cost effect of chlorine can be made as in Table 8.

E.g.: 16 ML/d plant and dosing 5 mg/L chlorine gas

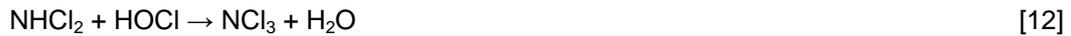
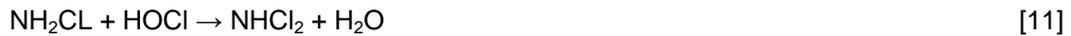
Table 8 – Chlorination operational cost

Chlorine required	3.33 kg/h
Cost as per chlorination graph (Figure 2)	R 400 000
Maintenance (3% per annum)	R 12 000
Electricity cost per annum	R 13 140
Personnel cost	Incl
Chlorine gas (R 10/kg)	R 292 000
Capital redemption (15 yrs, prime)	R 68 407
Total annual cost	R 385 547
Total annual kL produced	5 840 000 kL
Operational cost	6.60 c/kL

4.5 CHLORAMINATION

4.5.1 Basic chemistry

Chloramines are formed when chlorine and ammonia react. In solutions with a pH between 7.0 and 8.5 the chlorine species capable of reacting with ammonia form monochloramine, dichloramine and trichloramines (nitrogen trichloride) according to the equations below (USEPA, 1999). Ammonia is added as an ammonium hydroxide or ammonia gas.



The reactions are pH dependent (see Figure 3 below) and will degrade or form at varying pH levels. Monochloramine is the species most suited for drinking water disinfection. The other two chloramines cause taste and odour problems and should be avoided. A ratio of chlorine to ammonia in the range of 3:1 up to 5:1 is optimum for the formation of monochloramine (USEPA, 1999).

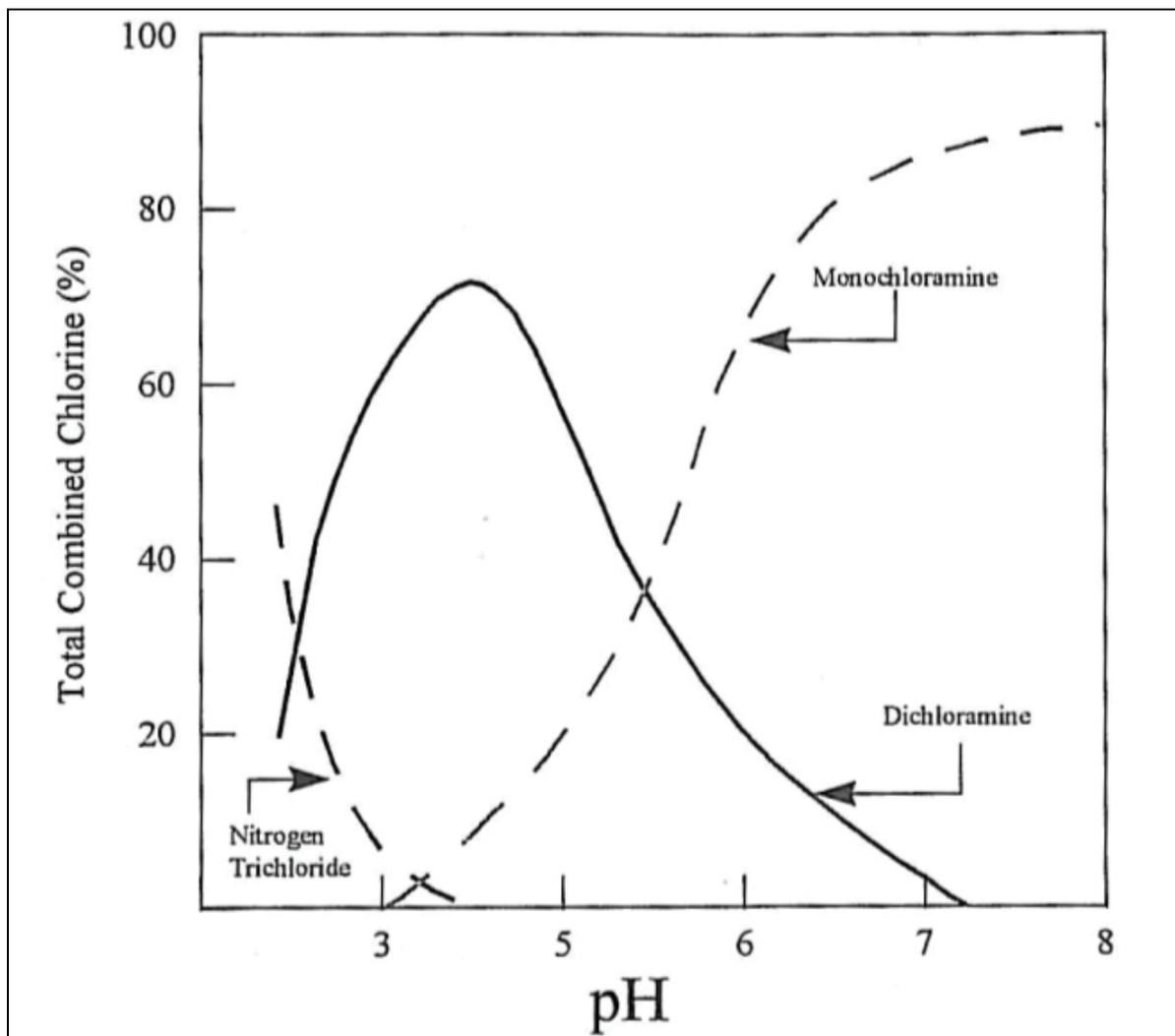


Figure 3 – Chloramine species as a function of pH (USEPA, 1999)

4.5.2 Oxidant demand

Iron and manganese must be oxidised to an insoluble form to remove them from the water. Due to the low oxidation potential of chloramines, this oxidant cannot oxidise iron, manganese or any organic component.

4.5.3 Disinfection demand

The mechanisms by which chloramines inactivate micro-organisms are believed to involve inhibition of proteins or protein mediated processes such as respiration. Because of the inconsistency in the rate of inactivation, monochloramines should have 'multiple hits' upon bacterial cells before cell death.

The CT values for *Giardia* cyst (Table 9) and virus (Table 10) inactivation using chloramines are given below. The values are valid for pH values between 6 and 9.

Table 9 – Contact time values for *Giardia* cyst inactivation (USEPA, 1999)

Inactivation	Temperature (°C) (mg.min/L)				
	5	10	15	20	25
0.5-log	365	310	250	185	125
1-log	735	615	500	370	250
1.5-log	1 100	930	750	550	375
2-log	1 470	1 230	1 000	735	500
2.5-log	1 830	1 540	1 250	915	625
3-log	2 200	1 850	1 500	1 100	750

Table 10 – Contact time values for virus inactivation (USEPA, 1999)

Inactivation	Temperature (°C) (mg.min/L)				
	5	10	15	20	25
2-log	857	643	428	321	214
3-log	1 423	1 067	712	534	356
4-log	1 988	1 491	994	746	497

4.5.4 Disinfection by-products

The chlorine-to-ammonia-ratio, the positions where ammonia and chlorine are added in relation to each other and the pH determine the DBP formation potential. Monochloramines do not produce DBPs to any significant degree, although some dichloroacetic acid can be formed. The formation of this compound has been found to be larger when monochloramines are used as secondary disinfectant instead of free chlorine.

Significantly less chlorinated organic materials are formed with the use of chloramines as a disinfection strategy and little is known about the nature of these by-products except that they are more hydrophilic and larger in molecular size than the organic halides produced from free chlorine.

4.5.5 Selection criteria (see selection chart)

For the typical water related problems as described in Chapter 3, the application of chloramine as an oxidant and disinfectant is as follows:

- i) High colour: Chloramines are generally not used for colour removal.
- ii) Taste and odour: Chloramines will not reduce taste and odour. An incorrectly controlled chlorine-nitrogen ratio actually can lead to the formation of undesirable chloramines species such as dichloramine and nitrogen trichloride. Both these species have a strong chlorinous smell even at low concentrations.
- iii) High manganese: Chloramines cannot oxidise manganese to an insoluble form.
- iv) High iron: Chloramines cannot oxidise iron to an insoluble form.
- v) High turbidity: Chloramines do not have an effect on the turbidity of treated water.
- vi) High algae: Chloramines are not effective in removing algae from water.
- vii) High chlorophyll: Chloramines are not effective in oxidising or bleaching chlorophyll-a.
- viii) High DOC: Chloramines are not effective in oxidising DOC or reducing DOC through other means.
- ix) High coliform: Chloramines are effective in the inactivation of coliform bacteria.
- x) High *Cryptosporidium*: Chloramines are ineffective in the disinfection of *Cryptosporidium*.
- xi) High *Giardia*: Chloramines are effective (at high CT values) for the inactivation of the *Giardia* cyst.
- xii) High cyanobacteria toxins: Chloramines are generally not applied to treat toxins.
- xiii) High ammonia: Ammonia is added after chlorine addition to form chloramines. If high ammonia is present during the chlorination process chloramines will already be formed by the time ammonia is added. Adding more ammonia will therefore lead to a non-ideal chlorine:nitrogen ratio.
- xiv) High COD: Chloramines cannot oxidise COD.

4.5.6 Environmental effects

External effects such as pH, temperature and the presence of organic and inorganic compounds have an effect on the disinfection properties of chloramines.

pH: The effect of pH has more to do with the organism than with the disinfectant; however, pH also controls the chloramine species distribution. Studies have indicated that the bactericidal properties of dichloramine were superior to that of monochloramine although it is qualified that pH may play a role due to the fact that changes in pH alter the physiological response of the organism. Other studies indicated that monochloramine is superior to dichloramine with regard to viricidal ability. Some evidence suggests that solutions containing approximately equal concentrations of monochloramine and dichloramine may be more microbiocidal than those containing only monochloramine or dichloramine.

Temperature: The bactericidal and viral inactivation efficiency of chloramine increases with increasing temperature. It is important to note that the efficiency dramatically decreases under conditions of high pH and low temperature. For example, the inactivation of *Escherichia coli* is approximately 60 times slower at pH 9.5 and temperatures between 2 and 6°C than at pH 7 and temperatures of 20-25°C.

4.5.7 Costs

Capital cost: The capital items required for a chloramines system include the items already mentioned for a chlorine dosing facility. Should a chloramines facility be planned from the start-up of a water treatment plant, the designer can take cognisance of the fact that generally less chlorine will be required than when a free chlorine system is planned. Depending on the distance of the reticulation system, it is not expected that monochloramine values higher than 2 mg/L will be required, which is significantly less than 3-5 mg/L of free chlorine normally utilised at plants for primary and secondary disinfection.

It is more common to find that plants using free chlorine are being converted to still practice free chlorine as primary disinfectant on site and using monochloramines as secondary disinfectant in the reticulation system. Items required for the addition of an ammoniation facility include the measurements of the free chlorine levels, dosing pumps of the ammonium hydroxide to the final water, a PLC system to control the dosing of ammonia, storage of the ammonia (either in gas cylinders or as a liquid) when aqueous ammonia is used. Figure 4 indicates typical costs as a function of the kg ammonia required per hour (2009 costs).

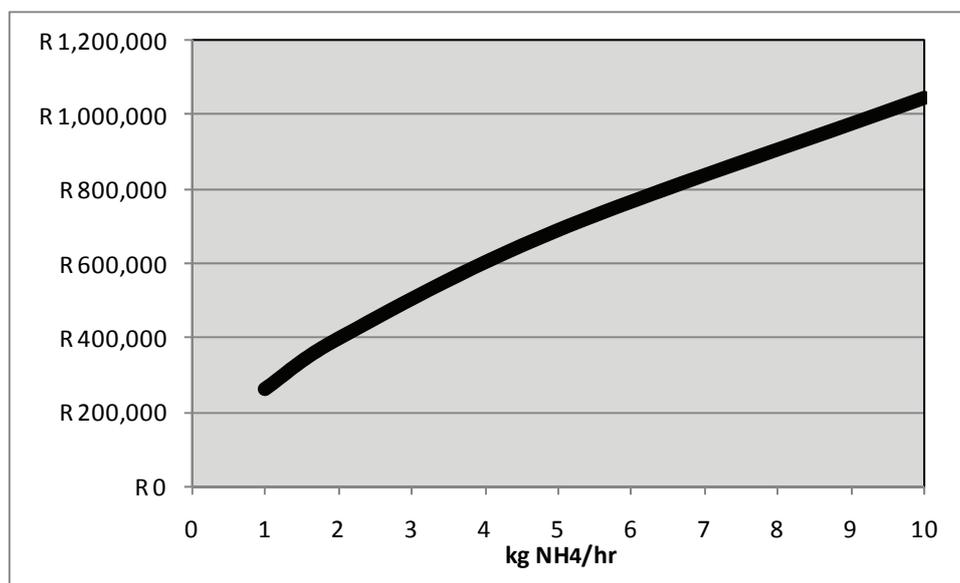


Figure 4 – Chloramination capital cost

Operational cost: The operational cost components consist of supply and delivery of the chemical, personnel cost, maintenance, electricity cost for the operation of the unit and capital redemption. An example is indicated below where a new plant is being planned and provision is made for new chlorine dosing equipment as well as new ammoniation dosing equipment. In this case, reference is made back to the chlorine graph indicated in Figure 2.

E.g. : 90 ML/d plant and dosing 4 mg/L chlorine gas and 1:4 ratio ammonia

Table 11 – Chloramination operational cost

Chlorine required	15.00 kg/h
Cost as per chlorination graph (Figure 2)	R 1 050 000
Ammonia required	1.875 kg/h
Cost as per chloramination graph (Figure 4)	R 350 000
Maintenance (3% per annum)	R 42 000
Electricity cost per annum	R 13 140
Personnel cost	Incl
Chlorine gas (R 10/kg)	R 1 314 000
Ammonia solution (R 6/kg N)	R 98 550
Capital redemption (15 yrs, prime)	R 239 424
Total annual cost	R 1 707 114
Total annual kL produced	32 850 000 kL
Operational cost	5.20 c/kL

4.5.8 Other considerations

The addition of monochloramines has impacts on other areas of a treatment facility and the following list highlights selected advantages and disadvantages of using chloramines (USEPA, 1999):

Advantages

- The addition of monochloramines upstream of filters will reduce biological growth on the filters. This implication has a positive and negative result. The filters will be kept cleaner and thus reduce backwash frequency. The undesirable impact is the reducing BDOC removal in filters that are run in biological mode.
- Chloramines are not as reactive with organics as free chlorine in forming DBPs.
- The monochloramine residual is more stable and longer lasting than free chlorine or chlorine dioxide.
- Because chloramines do not tend to react with organic compounds, many systems will experience fewer incidences of taste and odour complaints.
- Chloramines are inexpensive.

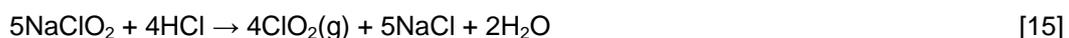
Disadvantages

- The ammonia used in the formation of chloramines provides nutrient ammonia for nitrifying bacterial growth. This growth can cause an increase in nitrate/nitrite levels in distribution systems. Excessive nitrification needs to be controlled by occasional shock dosing with chlorine.
- The ratio of the chlorine to the nitrate has to be monitored continuously to prevent formation of the other chloramine species and avoid excessive free ammonia.
- The disinfection properties of chloramines are not as strong as other disinfectants such as chlorine, ozone and chlorine dioxide.
- Chloramines cannot oxidise iron, manganese and sulphides.
- When using chloramine as the secondary disinfectant, it may be necessary to periodically convert to free chlorine for biofilm control in the water distribution system.
- Monochloramines are less effective as disinfectant at higher pH values.
- Chloramines must be produced on site.

4.6 CHLORINE DIOXIDE

4.6.1 Basic chemistry

Chlorine dioxide must be produced on-site because it is unstable at high concentrations. For potable water applications, chlorine dioxide is usually generated using a 25% sodium chlorite solution. A number of different approaches are then used to convert the chlorite to chlorine dioxide. These include reactions with gaseous chlorine (Cl_2) aqueous chlorine (HOCl) or acid (usually hydrochloric acid, HCl). The reactions are (MWH, 2005):



4.6.2 Oxidant demand

Relatively little has been published on the effectiveness of chlorine dioxide as an oxidant of iron and manganese in drinking water, but it is likely that it can be effective when Fe(II) is not strongly complexed with NOM. Studies with manganese indicated that the oxidation of Mn(II) is relatively rapid with the formation of colloidal particles of MnO₂. For oxidation of iron it has been reported that 1.21 mg chlorine dioxide is needed for every mg Iron in solution; the corresponding dose for manganese oxidation is 2.45 mg chlorine dioxide per mg Mn(II) (MWH, 2005).

Little information is available on the oxidation of hydrogen sulphide via chlorine dioxide, although rapid oxidation seems likely. Chlorine dioxide will also remove many of the swampy, grassy and fishy odours associated with drinking water, but like chlorine, it is of little use against the earthy musty odours associated with MIB and geosmin.

4.6.3 Disinfection demand

When the regulations of by-products of chlorination and ozone began, chlorine dioxide was a fairly high profile disinfection alternative. Almost no identifiable by-products, except a few aldehydes and ketones were produced at low levels (MWH, 2005). Since the formulation of the CT-concept, studies have been carried out into the inactivation of pathogens and Figures 5 and 6 indicate results on the CT requirements for *Giardia* cysts and viruses.

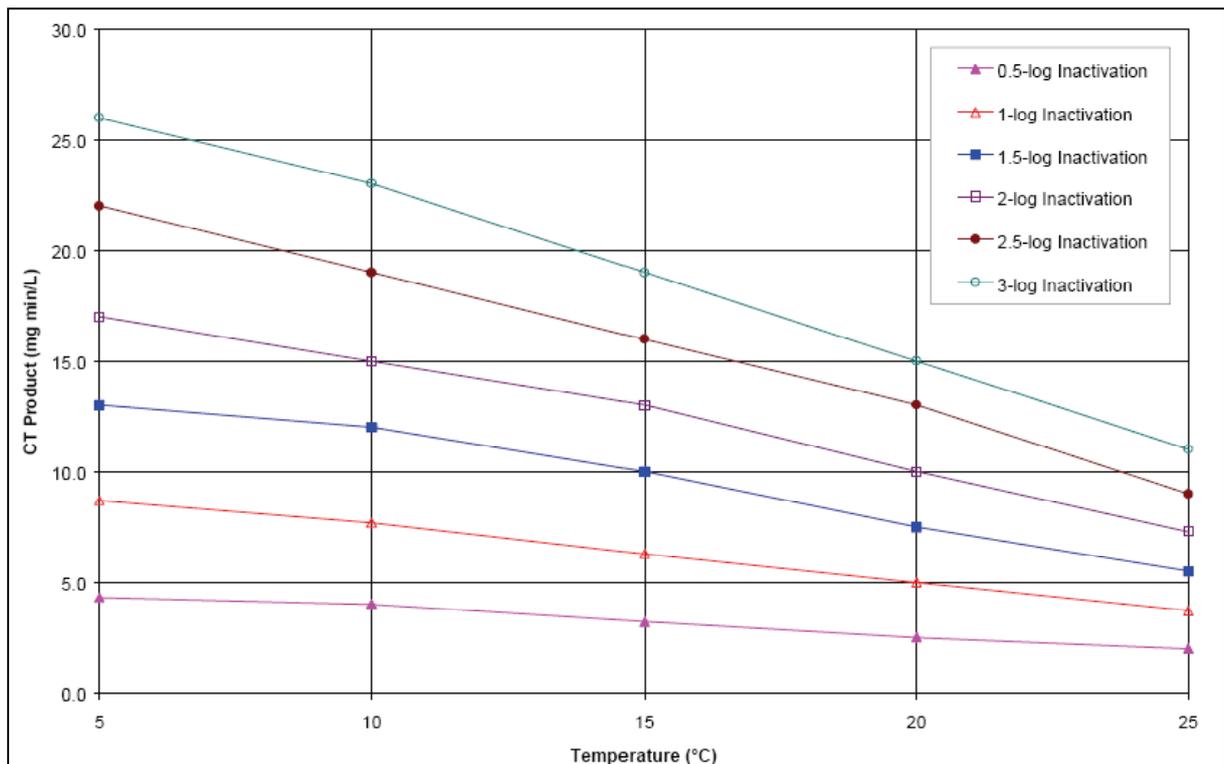


Figure 5 – Contact time values for *Giardia* cyst inactivation (USEPA, 1999)

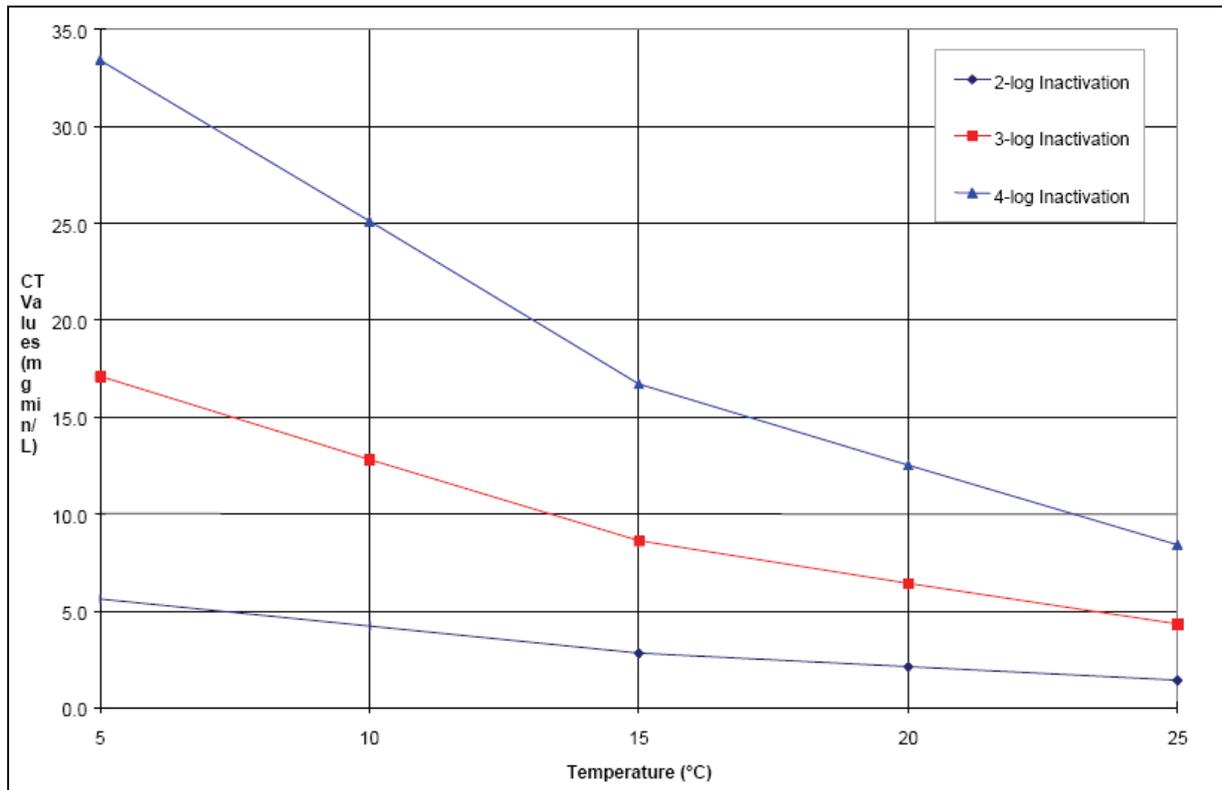


Figure 6 – Contact time values for virus inactivation (USEPA, 1999)

4.6.4 Disinfection by-products

Chlorine dioxide is known to produce two inorganic by-products, namely chlorite and chlorate. Late in the 1980s, concern on the toxicity of chlorite ion and chlorine dioxide itself reached a peak and when it was also discovered that the use of chlorine dioxide was sometimes responsible for the formation of a very undesirable ‘cat-urine’ odour, the State of California banned the use of this chemical as a disinfectant and several other states soon followed.

Eventually when the disinfectant by-product rule was promulgated in the US in 1998, a maximum disinfectant residual limit of 0.8 mg/L was set for chlorite ion and a MCL of 1 mg/L was set for chlorine dioxide. It was later established that the cat-urine odour only occurred when chlorite ion is exposed to a free chlorine residual.

It seems as if the use of chlorine dioxide may indeed play a role in minimising DBP formation and it has been shown that the formation of TTHMs and HAAs is reduced by using chlorine dioxide.

4.6.5 Selection criteria (see selection chart)

For the typical water related problems as described in Chapter 3, the application of chlorine as an oxidant and disinfectant is as follows:

- i) **High colour:** Chlorine dioxide can oxidise the double bonds which provide chromophoric properties to water, however, the dosages required might be prohibitive.
- ii) **Taste and odour:** Chlorine dioxide is effective in destroying tastes and odours produced by decaying vegetation, algae and phenolic compounds. These odours can be described as fishy and swampy. Chlorine dioxide is, however, not effective for the oxidation of geosmin and MIB.

- iii) High manganese: Chlorine dioxide effectively reacts with the soluble manganese to form a precipitate which can be removed through sedimentation and filtration.
- iv) High iron: Chlorine dioxide effectively reacts with the soluble iron to form a precipitate which can be removed through sedimentation and filtration.
- v) High turbidity: The removal of turbidity is a phase separation issue and chlorine dioxide will not aid in the removal of suspended solids. This technology is not effective if the aim is to remove turbidity.
- vi) High algae: Chlorine dioxide can effectively rupture algal cells which are thereafter removed by sedimentation and filtration.
- vii) High chlorophyll: As above, chlorine is effective in killing algae and will be able to bleach the chlorophyll afterwards.
- viii) High DOC: In general, chlorine dioxide is more effective than chlorine in minimising the formation of by-products associated with high DOC levels. It is still not advisable to use this disinfectant when high levels of NOM are present.
- ix) High coliform: Chlorine dioxide is effective in obtaining a 3-4 log removal of coliforms.
- x) High *Cryptosporidium*: Chlorine dioxide meets the requirements for <2.0 log removal but not for >2.0 log removal.
- xi) High *Giardia*: Chlorine dioxide is effective in the inactivation of *Giardia*.
- xii) High cyanobacteria toxins: Little study has been conducted on the effects of chlorine dioxide on microcystin degradation.
- xiii) High ammonia: Chlorine dioxide does not react with ammonia.
- xiv) High pathogen: As discussed under the pathogens, *Cryptosporidium* and *Giardia*, chlorine dioxide is effective for the inactivation of these pathogens.
- xv) High COD: For the purpose of mineralisation, chlorine dioxide as an oxidant is not effective.

4.6.6 Environmental effects

Studies on pH by Ridenour and Ingols (1947) indicated that the bactericidal activity of chlorine dioxide is unaffected by pH variations between 6 and 10. This is in marked contrast to the effect of pH on the efficiency of chlorine disinfection.

Similar to chlorine, the disinfection efficiency of chlorine dioxide decreases as temperature decreases (Mallet *et al.*, 1995). A 1997 study by LeChevallier *et al.* found that reducing the temperature from 20°C to 10°C reduced the disinfection effectiveness of chlorine dioxide on *Cryptosporidium* by 40%, which is similar to previous results for *Giardia* and viruses (USEPA, 1999).

Suspended matter and pathogen aggregation increase the water's turbidity and affect the disinfection efficiency of chlorine dioxide. Protection from chlorine dioxide inactivation due to bentonite was determined to be approximately 11% for turbidities equal to or less than 5 nephelometric turbidity units (NTU) and 25% for turbidities between 5 and 17 NTU (USEPA, 1999).

4.6.7 Costs

Capital cost

The capital items required for a chlorine dioxide system are associated with the establishment of a storage area for the chemicals required (particularly sodium chlorite). Then, depending on the mode of chlorine dioxide generation, provision must be made for the other chlorine substance (gas or acid). Since these are all hazardous chemicals, provision must be made for bunded areas to contain the chemicals in case of a spillage. From the storage area, the source chemicals must be blended in the correct ratio and the product stored (levels of about 5 g/L) for a short period from where dosing will take place. Dosing items will include the dosing pumps with associated piping and flow measurements

while a PLC system to control the whole process is often required. Figure 7 indicates typical costs as a function of the kg chlorine dioxide required per hour (2009 costs).

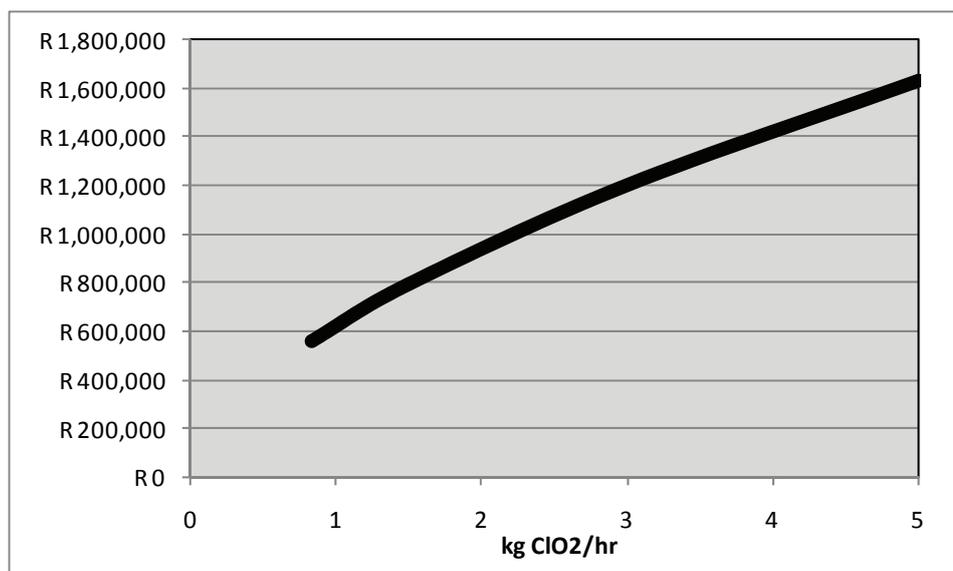


Figure 7 – Chlorine dioxide capital cost

Operational cost

The majority of the operational cost is created by the cost associated with generating this chemical. The capital redemption costs are small when compared to an effective chemical cost of some R 90/kg for the generation of chlorine dioxide. An example is indicated in Table 12 where a new 10 ML/d plant is being planned and provision is made for new chlorine dioxide dosing equipment for disinfection and oxidation of taste and odours.

E.g. 10 ML/d plant, dosing 2 mg/L chlorine dioxide

Table 12 – Chlorine dioxide operational cost

Chlorine dioxide required	0.83 kg/h
Cost as per chlorine dioxide graph (Figure 7)	R 550 000
Maintenance (3% per annum)	R 16 500
Electricity cost per annum	R 2 628
Personnel cost	Incl
Chlorine dioxide (R 90/kg)	R 657 000
Ammonia solution (R 6/kg N)	R 98 550
Capital redemption (15 yrs, prime)	R 94 059
Total annual cost	R 770 187
Total annual kL produced	3 650 000 kL
Operational cost	21.10 c/kL

4.6.8 Other considerations

The following list highlights selected advantages and disadvantages of using chlorine dioxide as a disinfectant for drinking water (USEPA, 1999). Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

Advantages

- Chlorine dioxide is more effective than chlorine and chloramines for inactivation of viruses, *Cryptosporidium* and *Giardia*.
- Chlorine dioxide oxidises iron, manganese, and sulphides.
- Chlorine dioxide may enhance the clarification process.
- Taste and odours resulting from algae and decaying vegetation, as well as phenolic compounds, are controlled by chlorine dioxide.
- Under proper generation conditions (i.e. no excess chlorine), halogen-substituted DBPs are not formed.
- Chlorine dioxide is easy to generate.
- Biocidal properties are not influenced by pH.
- Chlorine dioxide provides residuals in the water for prolonged protection.

Disadvantages

- The chlorine dioxide process forms the SPBs chlorite and chlorate.
- Generator efficiency and optimisation difficulty can cause excess chlorine to be fed at the application point, which can potentially form halogen-substitute DBPs.
- Costs associated with training, sampling, and laboratory testing for chlorite and chlorate are high.
- Equipment is typically rented, and the cost of the sodium chlorite is high.
- Chlorine dioxide decomposes in sunlight.
- Chlorine dioxide gas is explosive, so it must be made on-site.
- Chloride dioxide can lead to the production of noxious odours in some systems.

4.7 OZONE

Ozone is a gas at room temperature and is highly corrosive and toxic. The gas is colourless and has a pungent odour. Ozone is detectable at concentrations as low as 0.02 to 0.05 ppm. The detection limit is below health concerns. Ozone is a powerful oxidant and is capable of oxidising organic and inorganic compounds in water (USEPA, 1999).

4.7.1 Basic chemistry

Ozone often forms in nature under conditions where O_2 will not react. Ozone used in industry is measured in g/Nm^3 or weight percent. The regime of applied concentrations ranges from 1 to 5 weight percent in air and from 6 to 14 weight percent in oxygen. The formation of oxygen into ozone occurs with the use of energy. This process is carried out by an electric discharge field as in the CD-type ozone generators (corona discharge simulation of the lightning), or by ultraviolet radiation as in UV-type ozone generators (simulation of the ultraviolet rays from the sun). In addition to these commercial methods, ozone may also be made through electrolytic and chemical reactions. In general, an ozonation system includes passing dry, clean air through a high voltage electric discharge, i.e. corona discharge, which creates an ozone concentration of approximately 1% or 10 000 mg/L. This can be depicted as follows:



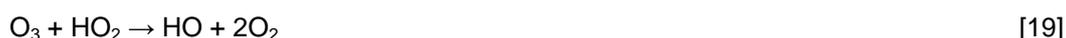
The concentration of ozone can be increased to as high as 14% by using an oxygen enriched feed gas such as liquid oxygen (LOX) or a concentrated air stream from a pressure swing adsorption (PSA) unit.

In water, ozone reacts with hydroxide ions (OH⁻) to form hydroxyl free radicals (HO•). Because the decay of the hydroxyl radicals is pH dependent, pH is a very important parameter in determining the concentration of ozone and hydroxyl radicals in solution and therefore the oxidation rates. Oxidation with ozone is also influenced by other water quality characteristics, such as temperature, alkalinity, and the concentration of reduced chemical species (i.e. iron and manganese). Other important considerations include ozone dose and contact time.

Ozone decomposition in water follows one of two reaction pathways:

- 1) direct oxidation, which is slow and selective in its oxidation of organic compounds, and
- 2) autodecomposition to the hydroxyl free radical (HO•), which is extremely fast and nonselective.

The hydroxyl free radical is scavenged by carbonate and bicarbonate ions, commonly measured as alkalinity, to form carbonate and bicarbonate free radicals. These radicals do not affect the organic reactions. The hydroxyl radicals produced by the autodecomposition react with organics and other radicals to reform hydroxyl radicals in an autocatalytic process. The decomposition of ozone in water is as follows:

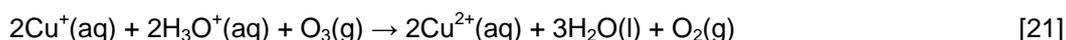


4.7.2 Oxidant demand

Ozone reacts with a number of organic and inorganic substances as follows:

Metals

Ozone will oxidise metals (except gold, platinum, and iridium) to oxides of the metals in their highest oxidation state, e.g.:



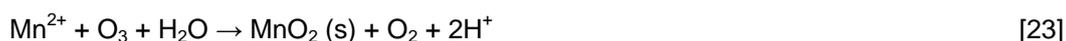
Iron



To oxidise the iron, 0.43 mg ozone is needed for every 1 mg of iron in solution.

Manganese

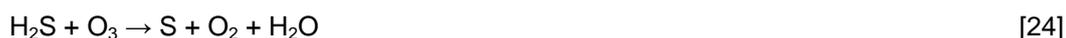
Ozone can be used to remove manganese from water, forming a precipitate which can be filtered:



For manganese oxidation, 0.88 mg ozone is needed for 1.0 mg manganese.

Sulphides

In an aqueous solution, two competing simultaneous reactions occur, one to produce elemental sulphur, and one to produce sulphuric acid:



Organic material

Ozone can mineralise organic material to CO₂:



The demand for ozone exerted by organics in the water has been proven by numerous studies to be between 0.5 to 1 mg O₃/mg DOC.

Ammonia

Ozone does not react with ammonium salts but it reacts with ammonia to form ammonium nitrate:



Cyanides

Ozone will oxidise cyanides to one thousand times less toxic cyanates:



Urea

Ozone will completely decompose urea.



4.7.3 Disinfection demand

Ozone is one of the most potent biocides used in water treatment. It is effective against a wide range of pathogenic microorganisms including bacteria, viruses, and protozoa. Ozone shows greater efficiency inactivating most types of pathogenic microorganisms than chlorine, chloramine, and chlorine dioxide (USEPA, 1999). This is demonstrated by the CT values found in the SWTR Guidance Manual presented in Table 13. The resistance of pathogenic microorganisms to ozone increases in the following order: bacteria, viruses, protozoa.

Table 13 – Comparison of CT values for chlorine and ozone (USEPA, 1999)

Log removal	Giardia						Viruses					
	<1°C		10°C		20°C		<1°C		10°C		20°C	
	Cl	O ₃	Cl	O ₃	Cl	O ₃	Cl	O ₃	Cl	O ₃	Cl	O ₃
0.5	40	0.48	21	0.23	10	0.12	-	-	-	-	-	-
1	79	0.97	42	0.48	21	0.24	-	-	-	-	-	-
2	158	1.9	83	0.95	41	0.48	6	0.9	3	0.5	1	0.25
3	237	2.9	125	1.43	62	0.72	9	1.4	4	0.8	2	0.4

Protozoan cysts are more resistant to ozone than bacteria and viruses. Data available for inactivation of *Cryptosporidium* oocysts suggest that, among protozoans, this pathogen is the most resistant to ozone. Studies have demonstrated that CT values may be as much as 25 times higher than those required for *Giardia*. These preliminary studies also demonstrate that CT requirements for *Cryptosporidium* inactivation increase by an average factor of approximately three for every 10°C

decrease in temperature. A summary of reported ozonation requirements for inactivation of *Cryptosporidium* and *Giardia* oocysts is presented in Table 14. The effect of temperature is also indicated (USEPA, 1999).

Table 14 – Log inactivation of *Giardia* and *Cryptosporidium* at different temperatures

Log inactivation	Crypto. CT at Temperature (°C) ¹			Giardia CT at Temperature (°C) ²			Multiplier at Temperature (°C) ³		
	1	13	22	1	13	22	1	13	22
0.5	12.0	3.1	2.0	0.48	0.19	0.10	25.0	16.3	20.0
1.0	24.0	6.2	3.9	0.97	0.38	0.21	24.7	16.3	18.6
1.5	36.0	9.3	5.9	1.50	0.58	0.31	24.0	16.0	19.0
2.0	48.0	12.0	7.8	1.90	0.76	0.42	25.3	15.8	18.6
2.5	60.0	16.0	9.8	2.40	0.95	0.52	25.0	16.8	18.8
3.0	72.0	19.0	12.0	2.90	1.14	0.62	24.8	16.7	19.4

¹Values reported to be acceptable for a pH range of 6 to 9, and are based on values developed by EPA in 2003

²*Giardia* CT required numbers are based upon the CT table included in the SWTG Guidance Manual

³Multiplier = *Crypto.* CT at a given temperature / *Giardia* at the same temperature

4.7.4 Disinfection by-products

Ozone does not produce chlorinated DBPs. Through the oxidation of natural organic precursor materials, however, ozone can alter the reactions between chlorine and NOM and affect the formation of chlorinated DBPs when chlorine is added downstream. Additionally, if bromide is present in the water supply, ozonation will create bromate, which is a regulated chemical. Ozonation of natural waters produces aldehydes, haloketones, ketoacids, carboxylic acids, and other types of biodegradable organic material which must be adequately controlled (often with a granular media biofilter) (USEPA, 1999).

Ozonation often increases the biodegradability of NOM in the treated water. Increasing biodegradability could be beneficial if a biological filtration process follows the ozonation step. A biological filtration step can remove the biodegradable fraction of NOM, increasing organic precursor removal. Biological filters remove NOM by using it as a substrate. Biological filtration can be employed on adsorptive media, such as granular activated carbon (GAC), and/or non-adsorptive media, such as sand and anthracite. Conversely, if the biodegradable fraction is not removed, it can increase the regrowth of microorganisms in the distribution system.

Ozone oxidises bromide to form hypobromous acid and hypobromite (HOBr and OBr⁻) under water treatment conditions. Hypobromite was found to be further oxidised to bromate or to a species that regenerates bromide, whereas HOBr reacts with NOM to form brominated organic by-products in waters containing bromide. Changes in pH can have a dramatic effect on the concentrations of HOBr and OBr⁻ and, therefore, the species of by-products formed. An increase in pH increases the relative concentration of Br⁻, which in turn leads to increased bromate formation. Reduced pH levels are often accompanied by a reduction in bromate concentrations; the lower pH enhances formation of bromoform and other organic brominated DBPs. It was found that the bromoform concentration first increased then diminished at higher ozone dosages, and it was also demonstrated that lower ozone dosage and longer contact time should produce less bromate than higher dosages and shorter contact times (USEPA, 1999).

Ozonation followed by chlorination has been observed to produce higher levels of haloketones than chlorination alone. Chloral hydrate occurs primarily as a result of chlorination, although ozonation followed by chlorination has been observed to increase levels beyond those observed with chlorination only. Ozonation followed by chlorination or chloramination can increase chloropicrin

levels above those observed with chlorination or chloramination alone. Ozonation followed by chloramination has been observed to increase cyanogen chloride levels beyond those observed with chloramination only. Cyanogen bromide, the brominated analogue of cyanogen chloride, has been detected after ozonation of water containing high bromide levels (USEPA, 1999).

Much less is known about non-halogenated DBPs than the halogenated organic compounds. Among the major ozonation by-products, aldehydes and carboxylic acids have the highest concentrations. Ozonation, followed by chlorination, has been found to yield the highest levels of acetaldehyde and formaldehyde. In addition, ozonation prior to chloramination is shown to produce more of these aldehydes than chloramination alone. The formation of ketoacids is proportional to the amount of DOC in the water. Ketoacid concentrations are largely unaffected by bromide concentration.

Ammonia addition has been used to limit the formation of some ozonation by-products and in one study bromoform concentrations decrease by approximately 30% when ammonia is added at a NH₃-to-ozone ratio of 1:4 mg/mg. The reason for this reduction is because HOBr reacts with ammonia to form bromamines, presumably making HOBr unavailable for reaction with NOM (USEPA, 1999).

4.7.5 Selection criteria (see selection chart)

- i) High colour: Ozone has a very high oxidation potential and has the ability to break the double bonds of colour molecules and is effective in the removal of colour.
- ii) Taste and odour: Ozone is effective in the removal of both taste and odour. It is however qualified in the sense that the environmental factors and specifically the pH of the water will affect the mode of oxidation. The removal of particularly geosmin and MIB is more susceptible to removal by means of the indirect mode of ozonation via the highly active hydroxyl radical.
- iii) High manganese: Ozone will effectively oxidise the soluble manganese ions to an insoluble manganese form.
- iv) High iron: Ozone will effectively oxidise the soluble iron ions to an insoluble iron form.
- v) High turbidity: Ozone has limited impact on turbidity, although some positive impacts have been found on turbidity reduction.
- vi) High algae: Ozone can rupture the cell wall of algae and effectively kill these compounds in the water
- vii) High chlorophyll: Ozone is an effective bleaching agent and is effective in removing chlorophyll-a from the water
- viii) High DOC: The ozone demand required by organic material is about 0.5-1 mg ozone per mg DOC. The ozone does not completely mineralise the organics but does change the composition of the organic molecule to a state which is more biodegradable. Ozone is effectively used to treat high organic composition waters.
- ix) High coliforms: Ozone is very effective in inactivating coliforms in water treatment.
- x) High *Cryptosporidium*: Ozone is effective in killing this pathogen.
- xi) High *Giardia*: Ozone can effectively inactivate this pathogen.
- xii) High cyanobacteria toxins: Ozone is effective in oxidising these toxins.
- xiii) High ammonia: Ozone is not effective in oxidising ammonia to nitrates and nitrites, although oxidation to ammonium nitrate does occur.
- xiv) High pathogen: Ozone is effective against pathogenic organisms like bacteria, protozoa and viruses.

- xv) High COD: Ozone should not be used when the objective is to oxidise high levels of organics to carbon dioxide.

4.7.6 Environmental factors

The stability of dissolved ozone is affected by pH, ultraviolet light, ozone concentration, and the concentration of radical scavengers (USEPA, 2005). Conditions of low pH favour the direct oxidation pathway, and high pH conditions favour the auto decomposition pathway described earlier. At pH levels between 3 and 6, the ozone is present primarily in its molecular form (O_3), and direct oxidation dominates. However, as the pH rises, the auto decomposition of ozone to produce the hydroxyl free radical ($HO\bullet$) becomes increasingly rapid. At pH levels greater than 10, the conversion of molecular O_3 to $HO\bullet$ is virtually instantaneous. In general, better disinfection would be expected at lower pH levels, since free hydroxyl radicals are short-lived compared to molecular ozone. Studies have shown that increasing the temperature from 0 to 30°C reduces the solubility of ozone and increases its decomposition rate (USEPA, 2005).

Temperature and alkalinity also affect formation of by-products during ozonation. Increased temperature will increase the levels of bromate, bromoform, and total organic bromide. It also increases the decomposition of ozone. Conversely, increasing alkalinity has been shown to reduce the formation of bromoform and total organic bromide, and increase the formation of bromate. Bicarbonate scavenges OH radicals, suggesting that the OH radical may play a role in the formation of brominated species by affecting the level of HOBr, which is presumed to be an active species for total organic bromide formation.

4.7.7 Costs

Capital cost: The civil works associated with an ozone facility comprise the contact tank and the storage buildings for the ozone equipment. The mechanical/electrical work associated with the ozone plant include the ozonators, the air preparation equipment (if an OSA or AIR system is required), the piping and ozone destructor units, the actual dosing equipment (radial diffusers, ceramic caps, static mixers, etc.), and all the associated instrumentation and control systems.

For the determination of the capital costs, two modes of ozone production have been established – one where ozone is generated from air or PSA units where some air preparation equipment is required, and another less expensive option where LOX is used as a source feed to the ozonators. In the latter case, the capital cost will be lower; but a higher operational cost will be experienced due to the purchasing of LOX as a chemical. Figure 8 indicates typical costs (at 2009 prices) as a function of the kg ozone required per hour.

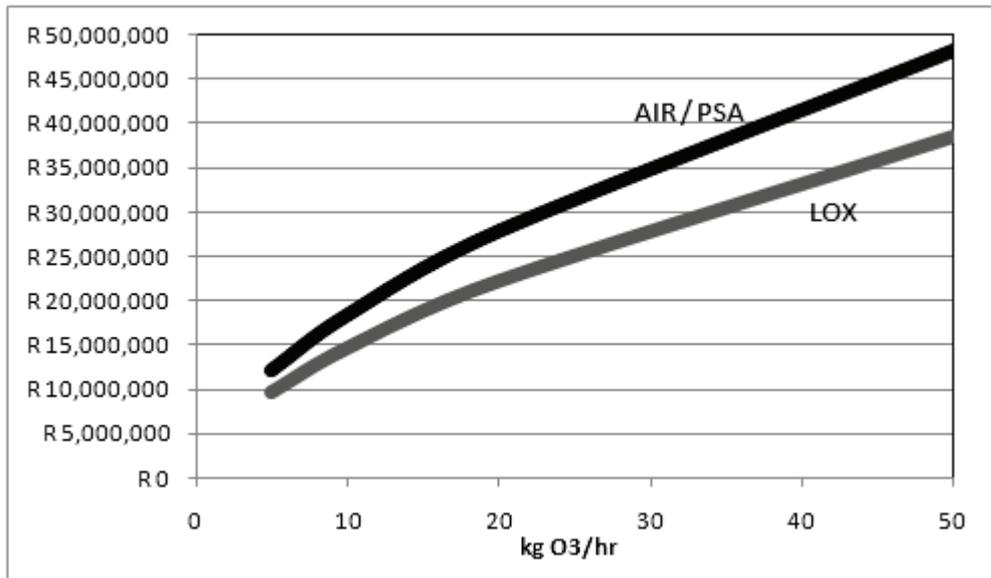


Figure 8 – Ozonation capital cost

Operational cost: Where energy and amortisation costs are the main driver for total operational costs at a PSA and air option, the main cost for a LOX system is based in the annual cost for LOX and the renting of the cryogenic tank. It has been shown at various times that the eventual effective cost of ozone works out to approximately R 30/kg when all aspects are taken into account. An example for a 40 ML/d ozone facility with ozone is indicated in Table 15.

E.g. : 40 ML/d plant and dosing 10 mg/L ozone

Table 15 – Ozonation operational cost

Ozone required	18.33 kg/h
Cost as per ozone graph (Figure 8)	R 26 000 000
Ozone (R 30/kg)	R 4 818 000
Total annual cost	R 4 818 000
Total annual kL produced	14 600 000 kL
Operational cost	33.00 c/kL

4.8 ULTRAVIOLET RADIATION

Ultraviolet radiation dissipates into water to be absorbed or reflected by material in the water. The absorption does not leave a residual, making a secondary disinfectant necessary. The radiation is present in the range of 100 to 400 nm electromagnetic waves. The optimum UV range for germicidal effects is between 245 and 285 nm (USEPA, 2005).

4.8.1 Basic chemistry

The destruction and inactivation of microorganisms is directly related to the UV dose. The UV dosage is calculated using the following equation:

$$D = I \times t$$

[30]

With D is the UV dose in $\text{mW}\cdot\text{s}/\text{cm}^2$, I the intensity in mW/cm^2 and t the exposure time in s. A constant fraction of microorganisms is deactivated when exposed to UV radiation. The dosage required for inactivation is site-specific and is related to the water quality and log removal requirements.

4.8.2 Oxidant demand

Ultraviolet radiation cannot oxidise inorganic or organic compounds.

4.8.3 Disinfection demand

Disinfection is accomplished by irradiating water with UV light, which alters the structure of the deoxyribonucleic acid (DNA) of the microorganisms in the treated water and thereby prevents the proper replication of the DNA strands. However, because microbes exposed to UV light still retain metabolic functions, some microbes are able to repair the damage done by the UV light and regain infectivity (USEPA, 2005).

Ultraviolet light is effective for the deactivation of bacterial and viral pathogens. For 2-log inactivation a UV dose of $21 \text{ mW}\cdot\text{s}/\text{cm}^2$ is required and for 3-log inactivation a UV dose of $36 \text{ mW}\cdot\text{s}/\text{cm}^2$ is required. Low dosages of UV are effective at inactivating viruses and bacteria, but much higher dosages are needed for *Cryptosporidium* and *Giardia*.

Ultraviolet light dose requirements are defined using IT values, which are the product of delivered UV intensity and the exposure time, and are analogous to CT values used to define chemical disinfectant dose. The data reported in the scientific literature illustrate the UV dose required to inactivate dispersed cultures of pathogens by various orders of magnitude. The UV dose used in a specific UV application will depend on the regulatory requirements for pathogen inactivation, the target pathogens, the number of microbes present, and the association of those microbes with particles.

Table 16 – Ultraviolet radiation requirements (USEPA, 1999)

Pathogen	Representative average UV dose (mWs/cm^2) required to inactivate			
	1-log	2-log	3-log	4-log
<i>Cryptosporidium parvum</i> oocysts	3.0	4.9	6.4	7.9
<i>Giardia lamblia</i> cysts	NA	<5.0	<10.0	<10.0
<i>Giardia muris</i> cysts	1.2	4.7	NA	NA
<i>Vibrio cholerae</i>	0.8	1.4	2.2	2.9
<i>Shigella dysenteriae</i>	0.5	1.2	2.0	3.0
<i>Escherichia coli</i> O157:H7	1.5	2.8	4.1	5.6
<i>Salmonella typhi</i>	1.8-2.7	4.1-4.8	5.5-6.4	7.1-8.2
<i>Shigella sonnei</i>	3.2	4.9	6.5	8.2
<i>Legionella pneumophile</i>	3.1	5.0	6.9	9.4
<i>Salmonella enteritidis</i>	5.0	7.0	9.0	10.0
Hepatitis A virus	4.1-5.5	8.2-14.0	12.0-22.0	16.0-30.0
Poliovirus Type 1	4.0-6.0	8.7-14.0	14.0-23.0	21.0-30.0
Coxsackie B5 virus	6.9	14.0	22.0	30.0
Rotavirus SA11	7.1-9.1	15.0-19.0	23.0-26.0	31-36
NA – Data not available				

4.8.4 Disinfection by-products

Several studies have been conducted to determine if DBPs are formed as a result of UV light irradiation. Zheng *et al.* (1999) found that THM and HAA9 formation did not increase when UV light was applied to chlorinated water at a dose of 100 mWs/cm². Linden *et al.* (1998) investigated DBP formation in wastewater secondary effluent that is irradiated with LP and MP UV lamps and found no evidence of photochemical reactions or DBP formation. Malley *et al.* (1995) examined the effects of post-UV disinfection (chlorination and chloramination) on DBP formation and found no significant impact by UV on DBP levels formed by chemical disinfection. Malley *et al.* (1995) also observed no significant change in THM, HAA, bromate, or other halogenated DBP concentrations following disinfection with UV light. A study performed with filtered drinking water indicated no significant change in aldehydes or carboxylic acids (Kashinkunti *et al.*, 2004).

However, several studies have shown low-level formation of non-regulated DBPs (e.g. aldehydes) as a result of applying UV light to wastewater and raw drinking water sources. The difference in results can be attributed to the difference in water quality, most notably the higher concentration of organic material in raw waters and wastewaters.

4.8.5 Selection criteria (See selection chart)

- i) High colour: UV is not effective in removing colour from the water due to the non-oxidative properties of the light.
- ii) Taste and odour: UV on its own is not able to remove tastes and odours from potable water.
- iii) High manganese: UV will not oxidise dissolved manganese to its solid state.
- iv) High iron: UV is not effective in oxidising dissolved iron.
- v) High turbidity: High turbidities have no impact on the effectiveness of UV during disinfection. UV has no effect on the turbidity of water.
- vi) High algae: UV has no effect on the killing of algae.
- vii) High chlorophyll: UV will not remove or bleach chlorophyll-a.
- viii) High DOC: UV has no effect on the removal of DOC in water.
- ix) High coliforms: UV is effective as a disinfectant for the removal of high coliforms in water.
- x) High *Cryptosporidium*: UV has been proven to be effective for the removal of this pathogen.
- xi) High *Giardia*: UV is effective in inactivation of this pathogen.
- xii) High cyanobacteria toxins: UV is not effective in the oxidation of these toxins.
- xiii) High ammonia: UV does not have an effect on high ammonia in the water.
- xiv) High pathogen: UV is used for the inactivation of pathogens (particularly in treated sewage water).
- xv) High COD: UV is not used for the treatment of high COD values in water.

4.8.6 Environmental effects

Particle content can impact UV disinfection performance. Particles may absorb and scatter light, thereby reducing the UV intensity delivered to the microorganisms. Particle-associated microbes also may be shielded from UV light, effectively reducing disinfection performance. Particles in source waters are diverse in composition and size and include large molecules, microbes, clay particles, algae, and flocs. For unfiltered raw waters, Passantino and Malley (2001) found that source water turbidity up to 10 NTU did not impact the UV dose-response of separately added (seeded) organisms.

Ultraviolet absorbance, often exerted by dissolved organic matter in drinking water applications, affects the design of the UV system. Water that absorbs a significant amount of UV light (i.e. high UV absorbance and low transmittance) will need a higher UV irradiance or longer exposure to achieve the same level of inactivation as water with lower UV absorbance. As UV absorbance increases, the intensity throughout the reactor decreases for a given lamp configuration. This results in a reduction in delivered dose and measured UV intensity for a given lamp output. Several chemicals used in water treatment processes can increase the UV absorbance of water (e.g., Iron (Fe^{+3})).

Depending on the water quality (e.g., dissolved ions, hardness, alkalinity, and pH levels) and lamp temperature, scale can form on the UV lamps. Medium pressure (MP) lamps tend to scale more easily than low pressure (LP) lamps because the operating temperature of MP lamps is considerably higher. Scale can reduce the UV energy being transmitted through the lamp sleeve into the water and potentially compromise disinfection. Lamp cleaning is an important consideration for the design of UV systems to control lamp scaling and to ensure consistent disinfection performance. Water pH may also affect lamp scale formation, but inactivation of microorganisms with UV light is not pH dependent (Malley, 1998).

Ultraviolet inactivation of microorganisms is not directly affected by water temperature. However, the performance of UV lamps is dependent on the lamp temperature. Most UV lamps have sleeves (usually made of quartz) that insulate the lamps, maintain optimal temperature, and provide maximum irradiance. If the lamp temperature deviates from optimal, the lamp irradiance will be reduced. This is especially true with LP UV lamps in cold waters. Therefore, the water temperature variation should be considered when designing a low pressure system. However, MP lamps have a significantly higher operating temperature compared to the water temperature. Thus, as long as an insulating quartz sleeve is in place, the water temperature has little effect on the operating temperature or performance of the MP lamp.

Hydraulics is an important part of the UV equipment. Ideally, the UV reactor should exhibit plug-flow characteristics. In plug flow, water that enters the reactor is completely mixed axially and moves through the reactor as a single plug with no dispersion in the direction of flow. However, 'real world' hydraulics in a full-scale reactor is never plug flow. Ultraviolet reactors are typically equipped with baffles to reduce the amount of short-circuiting through the reactor and to encourage plug flow, although these baffles can increase head loss through the reactor.

4.8.7 Costs

Capital Cost: The cost for a UV facility can vary significantly depending on the type of system installed and the purpose of the system. If it is to be installed at a sewage treatment facility for final disinfection before discharge to a water body, then contact is usually in a concrete tank with UV lamp in a suspended structure. With UV disinfection in potable water, it is often found that contact is by means of an inline facility in a pipeline. A typical facility's cost (at 2009 prices) where a dosage of 30 mWs/cm² with in-line units is indicated as an example in Figure 9.

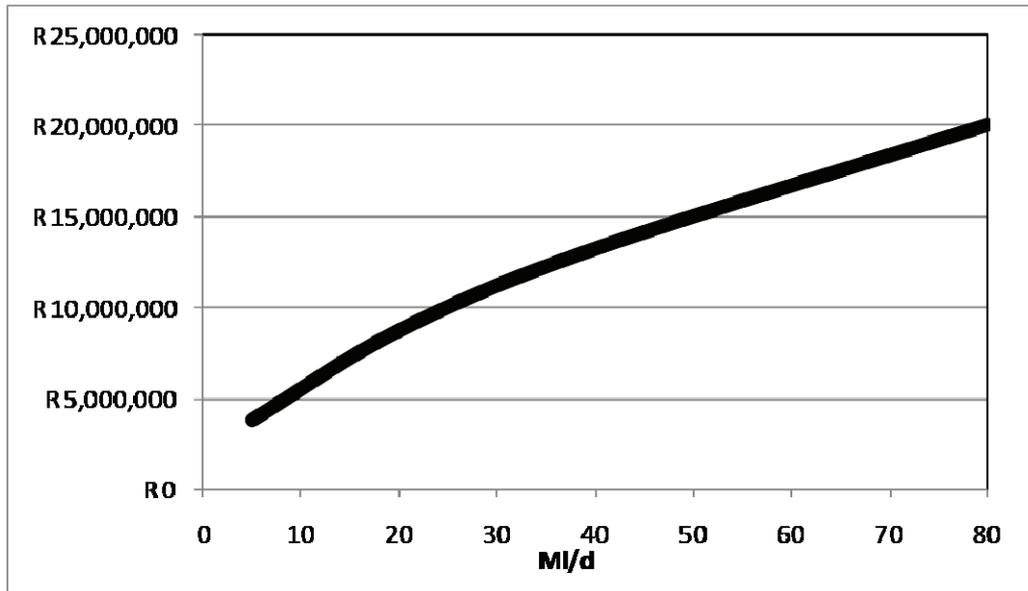


Figure 9 – Ultraviolet radiation capital cost

Operational Cost: The operational costs associated with a UV facility are indicated in Table 17.

E.g. : 41.6 ML/d plant with a UV dosage of 30 mWs/cm²

Table 17 – Ultraviolet radiation operational cost

Water flow to be treated	42.00 ML/d
Cost as per UV graph (Figure 9)	R 13 500 000
Maintenance (2% per annum)	R 270 000
Electricity requirement	R 86 569
Personnel cost	Incl
Lamp replacement	R 985 500
Capital redemption (15 yrs, prime)	2 308 730
Total annual cost	R 3 650 800
Total annual kL produced	15 176 700 kL
Operational cost	24.06 c/kL

4.9 POTASSIUM PERMANGANATE

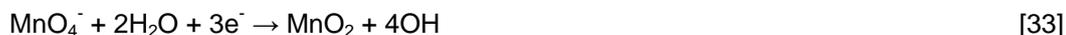
Potassium permanganate (KMnO₄) is used primarily to control taste and odours, remove colour, control biological growth in treatment plants and remove iron and manganese. In a secondary role, potassium permanganate may be useful in controlling the formation of THMs and other DBPs by oxidising precursors and reducing the demand for other disinfectants (MWH, 2005). The mechanism of reduced DBPs may be as simple as moving the point of chlorine application further downstream in the treatment train using potassium permanganate to control taste and odours, colour, algae, etc. instead of chlorine. Although potassium permanganate has many potential uses as an oxidant, it is a poor disinfectant.

4.9.1 Basic chemistry

The reactions are all exothermic, needing no energy to start. If the plant is operated at low pH values (acetic) the reactions are as follows:



If the plant is operated at high pH values (alkaline) then the reaction taking place is given by the equation below:



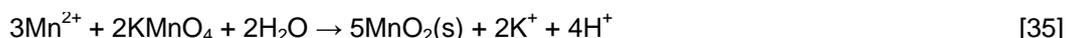
The reaction rates are dependent on the pH, dosage and temperature.

4.9.2 Oxidant demand

Although potassium permanganate can inactivate various bacteria and viruses, it is not used as a primary or secondary disinfectant when applied at commonly used treatment levels. Potassium permanganate is primarily used in drinking water treatment for the following applications:

- Oxidation of iron and manganese.
- Oxidation of taste and odour compounds.

Iron and manganese: Permanganate will oxidise iron and manganese to convert ferrous (2+) iron into the ferric (3⁺) state and 2⁺ manganese to the 4⁺ state. The oxidised forms will precipitate as ferric hydroxide and manganese hydroxide; the precise chemical composition of the precipitate will depend on the nature of the water, temperature, and pH. The reactions are:



These reactions show that alkalinity is consumed through acid production at the rate of 1.49 mg/L as CaCO₃ per mg/L of Fe²⁺ and 1.21 mg/L as CaCO₃ per mg/L of Mn²⁺ oxidised. This consumption of alkalinity should be considered when permanganate treatment is used along with alum coagulation, which also requires alkalinity to form precipitates.

The potassium permanganate dose required for oxidation is 0.94 mg/mg iron and 1.92 mg/mg manganese. In practice, the actual amount of potassium permanganate used has been found to be less than that indicated by stoichiometry. It is thought that this is because of the catalytic influence of MnO₂ on the reactions. The oxidation time ranges from five to ten minutes, provided that the pH is over 7.0.

Taste and odours: It has been reported that potassium permanganate can be used to remove taste and odour causing compounds such as earthy-musty smelling compounds in drinking water. Dosages of potassium permanganate used to treat taste and odour causing compounds range from 0.25 to 20 mg/L (USEPA, 1999).

4.9.3 Disinfection demand

While not considered a primary disinfectant, potassium permanganate has an effect on the development of a disinfection strategy by serving as an alternative to pre-chlorination or other oxidants at locations in a treatment plant where chemical oxidation is desired for control of colour, taste and odour, and algae.

The primary mode of pathogen inactivation by potassium permanganate is direct oxidation of cell material or specific enzyme destruction (USEPA, 1999). In the same fashion, the permanganate ion (MnO_4^-) attacks a wide range of microorganisms such as bacteria, fungi, viruses, and algae. Application of potassium permanganate results in the precipitation of manganese dioxide. This mechanism represents an additional method for the removal of microorganisms from potable water. In colloidal form, the manganese dioxide precipitant has an outer layer of exposed OH groups. These groups are capable of adsorbing charged species and particles in addition to neutral molecules. As the precipitant is formed, microorganisms can be adsorbed into the colloids and settled.

Bacteria inactivation: Early research showed that a dose of 2.5 mg/L was required for complete inactivation of coliform bacteria (USEPA, 1999). In this study, water from the Marne River was dosed with potassium permanganate at concentrations of 0 to 2.5 mg/L.

The USEPA (1999) also reports on the disinfectant ability of potassium permanganate on several waterborne pathogenic microorganisms. The investigation studied *Vibrio cholerae*, *Salmonella typhi*, and *Bacillus dysenteriae* (formerly *Bacteria flexner*). The results indicated that doses of 20 mg/L and contact times of 24 hours were necessary to deactivate these pathogens; however, even under these conditions the complete absence of *S. typhi* or *B. dysenteriae* was not assured, even at a potassium permanganate concentration that turned the water an objectionable pink colour.

Results from a study conducted in 1976 at the Las Vegas Valley Water District/Southern Nevada System of Lake Mead water showed that complete removal of coliform bacteria was accomplished at doses of 1, 2, 3, 4, 5, and 6 mg/L (USEPA, 1999). Contact times of 30 minutes were provided with doses of 1 and 2 mg/L, and 10 minutes contact times were provided for higher dosages in this study.

Virus inactivation: Potassium permanganate has been proven effective against certain viruses. A dose of 50 mg/L of potassium permanganate and a contact time of 2 hours was required for inactivation of poliovirus (strain MVA) (USEPA, 1999). A potassium permanganate dose of 5.0 mg/L and a contact time of 33 minutes were needed for 1-log inactivation of type 1 poliovirus. Tests showed a significantly higher inactivation rate at 23°C than at 7°C; but there was no significant difference in activation rates at pH 6.0 and pH 8.0.

Potassium permanganate doses from 0.5 to 5 mg/L were capable of obtaining at least a 2 log inactivation of the surrogate virus, MS-2 bacteriophage with *E. coli* as the host bacterium. Results showed that at pH 6.0 and 8.0, a 2-log inactivation occurred after a contact time of at least 52 minutes and a residual of 0.5 mg/L. At a residual of 5.0 mg/L, approximately 7 and 13 minutes were required for 2-log inactivation at pH values of 8.0 and 6.0, respectively. These results contradict the previously cited studies that potassium permanganate becomes more effective as the pH decreases.

Protozoa inactivation: No information pertaining to protozoa inactivation by potassium permanganate is available in the literature. However, based on the other disinfectants discussed in this report, protozoa are significantly more resistant than viruses; and so it is likely that the dosages and contact times required for protozoa inactivation would be impractical. Table 18 provides the CT values required for the inactivation of the MS-2 bacteriophage (USEPA, 1999)

Table 18 – MS-2 bacteriophage inactivation using $KMnO_4$

Residual (mg/L)	pH 6.0 (mg min/L)	pH 8.0 (mg min/L)
0.5	27.4	26.1
1.5	32.0	50.9
2.0	-	53.5
5.0	63.8	35.5

4.9.4 Disinfection by-products

At present no literature is available to specifically address DBPs with regard to potassium permanganate usage. It is anticipated that potassium permanganate may play a role in disinfection and DBP control strategies in water treatment. Potassium permanganate could be used to oxidise organic precursors at the head of the treatment plant minimising the formation of by-products at the downstream disinfection stage of the plant. Test results from a study conducted at two water treatment plants in North Carolina showed that pre-treatment with permanganate reduced chloroform formation; however, the reduction was of limited significance when applying dosages typically used at water treatment plants. The study also indicated that pre-oxidation with permanganate had no net effect on the chlorine demand of the water.

4.9.5 Selection criteria (see selection chart)

- i) High colour: Potassium permanganate is effective at colour removal as long as concentrations stay low and there is no residual permanganate, which forms a pink colour in the water.
- ii) Taste and odour: Potassium permanganate is used in the removal of both taste and odour.
- iii) High manganese: Potassium permanganate is effective at the oxidation of dissolved manganese in water.
- iv) High iron: Potassium permanganate is effective at the oxidation of dissolved iron in water.
- v) High turbidity: Potassium permanganate is not effective in treatment of turbidity.
- vi) High algae: Potassium permanganate is effective in the control and killing of algae in water
- vii) High chlorophyll: Potassium permanganate is not effective for the oxidation and bleaching of chlorophyll-a.
- viii) High DOC: Potassium permanganate will oxidise organic content in the water but is not commonly used for the oxidation and treatment of water containing a high amount of organic material.
- ix) High coliforms: Potassium permanganate can be used for the disinfection of bacteria; however it is not commonly used for this purpose.
- x) High *Cryptosporidium*: Potassium permanganate is not effective for the inactivation of *Cryptosporidium*.
- xi) High *Giardia*: Potassium permanganate is not effective for the inactivation of *Giardia*.
- xii) High cyanobacteria toxins: Potassium permanganate is not effective for the oxidation and treatment of these toxins
- xiii) High ammonia: Potassium permanganate is not effective for the oxidation of ammonia.
- xiv) High COD: Potassium permanganate can be used for the lowering of COD; however, this is not common practice.

4.9.6 Environmental effects

The inactivation efficiency depends upon the permanganate concentration, contact time, temperature, pH, and presence of other oxidisable material. Several of the key parameters are discussed below.

pH: Alkaline conditions enhance the capability of potassium permanganate to oxidise organic matter; however the opposite is true for its disinfecting power. Typically, potassium permanganate is a better biocide under acidic conditions than under alkaline conditions (USEPA, 1999). Results from a study conducted in 1964 indicated that permanganate generally was a more effective biocide for *E. coli* at lower pH levels, exhibiting more than a 2-log removal at a pH of 5.9 and a water temperature of both

0 and 20°C. A study conducted at the University of Arizona found that potassium permanganate will inactivate *Legionella pneumophila* more rapidly at pH 6.0 than at pH 8.0 (USEPA, 1999).

Temperature: Higher temperatures slightly enhance bactericidal action of potassium permanganate. The results from a study conducted on polio virus showed that oxidation inactivation is enhanced by higher temperatures. These results are consistent with results obtained for *E. coli* inactivation.

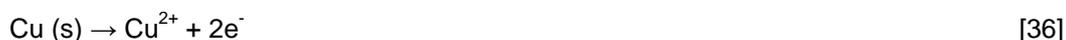
Dissolved organics and inorganics: The presence of oxidisable organics or inorganics in the water reduces the disinfection effectiveness of this disinfectant because some of the applied potassium permanganate will be consumed in the oxidation of organics and inorganics. Permanganate oxidises a wide variety of inorganic and organic substances in the pH range of 4 to 9. Under typical water conditions, iron and manganese are oxidised and precipitated, and most contaminants that cause odours and tastes, such as phenols and algae, are readily degraded by permanganate.

4.10 COPPER - SILVER IONISATION

Copper and its alloys (brasses, bronzes, copper nickels, copper nickel zincs, and others) are inherently antimicrobial materials. Man exploited the antimicrobial attributes of copper long before the nineteenth century, when Louis Pasteur developed the germ theory of disease which states that infections are caused by microbes invading the human body. Egyptians used copper drinking vessels to sterilise water. The Hippocrates Collection, 460 to 380 B.C., to which the father of medicine contributed, recommended the use of copper for leg ulcers related to varicose veins. Pliny, 23 to 79 A.D., used copper oxide with honey to treat intestinal worms. The Aztecs gargled with a mixture containing copper to treat sore throats and the Vikings used copper strings on their ships to prevent the growth of algae and shells. Modern ships still use the same technology; some anti-fouling paints contain copper, reducing the number of marine species growing on the walls of ships. Nomads used silver coins to improve drinking water quality. Since 1869 various publications have appeared on disinfection properties of silver. Some European and Russian villages have been using silver for drinking water treatment for many years (Faust and Aly, 1998).

4.10.1 Basic chemistry

Copper and silver ionisation are brought about by electrolysis. An electric current is created through copper-silver, causing positively charged copper (Cu^+ and Cu^{2+}) and silver (Ag^+) ions to form. The electrodes are placed close together and the water that is disinfected flows past the electrodes where an electric current is created, causing the outer atoms of the electrodes to lose an electron and become positively charged. The larger part of the ions flows away through the water, before reaching the opposite electrode. The reactions are:



4.10.2 Oxidant demand

Copper has no oxidative properties.

4.10.3 Disinfection demand

Electrically charged copper ions (Cu^{2+}) in the water search for particles of opposite polarity, such as bacteria, viruses and fungi. Positively charged copper ions form electrostatic compounds with negatively charged cell walls of microorganisms. These compounds disturb cell wall permeability and cause nutrient uptake to fail. Copper ions penetrate the cell wall and as a result they will create an entrance for silver ions (Ag^+). These penetrate the core of the microorganism. Silver ions bond to various parts of the cell, such as the DNA and RNA, cellular proteins and respiratory enzymes, causing all life support systems in the cell to be immobilised. As a result, there is no more cellular growth or cell division, causing bacteria to no longer multiply and eventually die out. The ions remain active until they are absorbed by a microorganism.

Other theories for copper disinfection:

- Causes leakage of potassium or glutamate through the outer membrane of bacteria.
- Disturb osmotic balance.
- Binds to proteins that do not require copper.
- Cause oxidative stress by generating hydrogen peroxide.

Copper-silver ionisation can deactivate *Legionella* bacteria and other microorganisms in slow-running and still water. *Legionella* spp. are very susceptible to copper and silver ionisation. Copper-silver ionisation can also disinfect biofilms. The deactivation rate of copper-silver ionisation is lower than that of ozone or UV. One benefit of copper-silver ionisation is that ions remain in the water for a long period of time. This causes long-term disinfection and protection from recontamination.

For effective disinfection to take place, *Legionella* bacteria in potable water need to be in contact with Cu^{2+} ions in concentrations of 0.1 to 1 mg/L for several hours. Copper levels for other applications do not have to be high and 0.3 to 0.5 mg/L usually is sufficient to help control algae and render many bacteria non-viable.

Laboratory studies conducted under USEPA-approved protocols have proven copper's ability to kill common bacteria including *Staphylococcus aureus*, *Enterobacter aerogenes*, *Escherichia coli*, *Pseudomonas aeruginosa* and methicillin-resistant *Staphylococcus aureus* (MRSA) within two hours of contact time. These studies were conducted using copper, stainless steel and plastic materials as surface areas where bacteria commonly accumulate in hospital conditions.

Low levels of silver in water are required for disinfection purposes as shown in Table 19.

Table 19 – Disinfection demand for Ag ionisation

Water source	µg/L
Drinking water and mineral waters	25-100
Water in swimming pools	150-200
Water to make artificial ice	400
Water for washing dishes and utensils in factories preparing food articles	25-600

4.10.4 Disinfection by-products

Insufficient evidence has been found regarding the possible health effects of long-term exposure to copper-silver ionisation. The European Union does not dictate any standards considering silver concentrations in water. Copper, however, has a maximum value of 20 µg/L, because it corrodes waterworks. The WHO does not dictate any standards considering the concentration of silver as a

drinking water disinfectant, because the organisation found the available data to be insufficient to recommend a health standard (WHO, 2008). The USA dictates maximum values of 1 mg/L of copper and a 0.1 mg/L of silver.

4.10.5 Selection criteria (see selection chart)

- i) High colour: Copper - silver ionisation has no effect on the colour of the water.
- ii) Taste and odour: Copper - silver ionisation has no effect on the odour or taste.
- iii) High manganese: Copper - silver ionisation has no effect on the oxidation of manganese.
- iv) High iron: Copper - silver ionisation has no effect on the oxidation of iron.
- v) High turbidity: Copper - silver ionisation has no effect on turbidity values.
- vi) High algae: Copper - silver ionisation inactivates the DNA/RNA of algae, rendering their life support systems useless.
- vii) High chlorophyll: Copper - silver ionisation do not have the ability to bleach or oxidise chlorophyll-a.
- viii) High DOC: Copper - silver ionisation do not have the ability to oxidise organics in the water which leads to high levels of DOC.
- ix) High coliforms: Copper is more effective than silver for the general inactivation of bacteria and viruses; however, a long contact time is required.
- x) High *Cryptosporidium*: Copper may have some biocidal effects on *Cryptosporidium*; however, high dosage and a long contact time are required. Silver is not effective.
- xi) High *Giardia*: Copper may have some biocidal effects on *Giardia*; however, high dosage and a long contact time are required. Silver is not effective.
- xii) High cyanobacteria toxins: Copper - silver ionisation is not effective for the oxidation of these toxins.
- xiii) High ammonia: Copper - silver ionisation is not effective for the removal of high levels of ammonia.
- xiv) High COD: Copper - silver ionisation is not effective in the treatment of high levels of COD.

4.10.6 Environmental effects

The effectiveness of copper-silver disinfection depends on a number of factors:

1. The concentration of copper and silver ions in the water should be sufficient for disinfection. The required concentration is determined by the water flow, the volume of water in the system, the conductivity of the water and the present concentration of microorganisms.
2. The electrodes should be in good condition. When the water is hard or fouling takes place as a consequence of water hardness and quality, there will be a decrease in electrode release and the additional effect will decrease. By using pure silver and pure copper, the supply of copper and silver ions can be regulated separately. These electrodes suffer from less limestone formation and fouling.
3. The effectiveness of copper-silver ionisation depends on the pH value of the water. When pH values are high, copper ions are less effective. When the pH value exceeds 6, insoluble copper complexes will precipitate. When the pH value is 5, copper ions mainly exist as $\text{Cu}(\text{HCO}_3)^+$; when the pH value is 7, as $\text{Cu}(\text{CO}_3)$ and when the pH value is 9, as $\text{Cu}(\text{CO}_3)^{2-}$.

4. Copper-silver ionisation effectiveness is determined by the presence of chlorine. Chlorine causes a silver-chlorine complex formation. When this occurs, silver ions are no longer available for disinfection.

4.10.7 Costs

Installation of the system requires two metal probes (rods or plates), one copper and one silver. A current has to be supplied over these two probes from an AC/DC converter. In hard water systems the probes should be cleaned regularly and thoroughly to avoid scaling from lime. Costs vary in the industry depending on the agent and area of application, and the consumer is advised to contact various suppliers to determine the most cost-effective installation.

4.11 ADVANCED OXIDATION PROCESSES

Water quality is becoming an increasingly important issue around the world. Pollution of both ground water and surface water has resulted from the disposal of pharmaceuticals, personal care products and industrial wastes into our water supplies. Often the contaminants are found in low concentrations and are very difficult to remove by conventional means. Even when conventional methods do work, e.g., with activated carbon treatment, we are simply moving the pollutant from the water to the carbon which must be disposed of in a safe manner. In recent years, advanced oxidation processes (AOPs) have been developed that can treat these pollutants without further disposal issues.

An AOP combines multiple oxidants like ozone and hydrogen peroxide to form a much stronger oxidant known as the hydroxyl radical. This compound is capable of oxidising virtually any organic compound. There is a variety of AOPs such as UV and ozone, UV and peroxide, peroxide and ozone, peroxide with various catalysts, etc. UV with ozone is an intriguing combination since the ozone can be made from air and the entire process does not require any purchase or storage of chemicals. The oxidants are produced on site, and with proper design produce no by-products. All AOPs are designed to produce hydroxyl radicals. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds. Table 20 shows the oxidising power of hydroxyl radicals and other oxidants.

Table 20 – Oxidising agents

Oxidising agent	EOP (mV)	EOP vs. Cl ₂
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

The most widely applied AOPs have been:

- Peroxide/ultraviolet light (H₂O₂/UV).
- Ozone/ultraviolet light (O₃/UV).
- Hydrogen peroxide/ozone (H₂O₂/O₃).
- Hydrogen peroxide/ozone/ultraviolet (H₂O₂/O₃/UV) processes.
- Fenton's reagent with ozone and/or UV.

Ultraviolet, ozone, peroxide advanced oxidation

Variations on the basic schemes of creating hydroxyl radicals using UV and either ozone or peroxide can be combined to use all three components.

The most direct method for the generation of hydroxyl radicals is through cleavage of hydrogen peroxide. Photolysis of H₂O₂ is known to yield hydroxyl radicals by a direct process, i.e. with a quantum yield of two OH radicals formed per quantum of radiation adsorbed (van der Walt, 1997).



The method of adding the oxidants at different points of the process or in different combinations is designed to improve the efficiency of the overall oxidation process. The idea is to improve both the economy of hydroxyl radical production as well as the economy of hydroxyl radical use. As a simple example, if one of the species that one wants to oxidise is readily oxidised by peroxide, it does not make economic sense to oxidise it using an expensive species such as the hydroxyl radical. Instead, by introducing peroxide first, one can oxidise this easier to oxidise species prior to introduction of the hydroxyl radicals. Excess peroxide can then be reacted with UV or ozone to form hydroxyl radicals for the attack of the more difficult to oxidise species.

Ultraviolet / ozone advanced oxidation process

In the UV / ozone process, photons in the UV spectrum convert ozone in the presence of water to oxygen and peroxide. The peroxide then reacts with the ozone to form the hydroxyl radical. A simplified reaction sequence is shown below:



The advantages and disadvantages of the O₃/UV system are:

- The removal efficiency of the combined O₃/UV process is typically higher than the combined removal efficiencies of ozone and UV alone.
- The combined O₃/UV process is more efficient at generating hydroxyl radicals than the combined H₂O₂/UV process for equal oxidant concentrations using LP-UV. This is because the molar extinction coefficient of O₃ at 254 nm is two orders of magnitude greater than that of H₂O₂, indicating that a lower UV intensity or a higher H₂O₂ dose is required to generate the same number of hydroxyl radicals for these two processes.
- For MP-UV lamps however, H₂O₂/UV processes will generate more hydroxyl radicals than O₃/UV processes.
- Despite the fact that O₃/UV is more stoichiometrically efficient than H₂O₂/UV or H₂O₂/O₃ at generating hydroxyl radicals, the O₃/UV process is less energetically efficient than H₂O₂/UV or H₂O₂/O₃ for generating large quantities of hydroxyl radicals due to the low solubility of O₃ in water compared to H₂O₂. Thus, operational costs are expected to be higher if large amounts of contaminant are present.

Peroxide / ozone (peroxone)

In an H₂O₂/O₃ system, H₂O₂ is used in conjunction with O₃ to enhance the formation of hydroxyl radicals via the reaction described by Equations [42] and [43].



Ozone is dosed at a ratio of 1 to 2 mg/L ozone per mg/L DOC; however, higher dosages are recommended for source waters with high alkalinity (>100 mg/L as CaCO₃), or NOM. H₂O₂ is fed from an aqueous solution at peroxide to ozone ratios ranging from 0.3:1 to 3:1. The specific ratio will be a function of disinfection requirements, bromide concentration, contaminant concentration, and other water quality parameters.

The combined H₂O₂/O₃ process has been demonstrated to be more effective at removing natural and synthetic organics than O₃ or H₂O₂ alone. In addition, using a combination of O₃ and H₂O₂ to produce hydroxyl radicals, rather than just O₃, allows a lower dosage of O₃ to be used.

The theoretical yield of hydroxyl radicals via H₂O₂/O₃ technology is less than that of the H₂O₂/UV technology; however, the yield is less affected by water quality (i.e. turbidity, iron, and nitrates lower the yield for UV processes, but not for H₂O₂/O₃ processes).

Fenton's reagent

Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidise contaminants or waste waters. Fenton's reagent can be used to destroy organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE). It was developed in the 1890s by Henry John Horstman Fenton (USEPA, 1999).

As described by Equation [44], ferrous iron(II) is oxidised by hydrogen peroxide to ferric iron(III), a hydroxyl radical and a hydroxyl anion. Iron(III) is then reduced back to iron(II), a peroxide radical and a proton by the same hydrogen peroxide (disproportionation) as shown in Equation [45].



The first reaction was first suggested by Haber and Weiss in the 1930s, but is commonly referred to as 'the Fenton reaction'. In the net reaction the presence of iron is truly catalytic and two molecules of hydrogen peroxide are converted into two hydroxyl radicals and water. The generated radicals then engage in secondary reactions. Iron(II) sulphate is a typical iron compound in Fenton's reagent.

4.11.1 Oxidant demand

Advanced oxidation processes have a wide range of applications, mainly for oxidation of refractory compounds, TOC and COD reduction in:

- Gas effluent treatment.
- Water reclaim / reuse / recycling.
- Drinking water supplies.
- Industrial & municipal wastewater.
- Process water, ultra-pure water.
- Electronic & pharmaceutical industries.
- Medicinal baths, sanatoria, hospitals.
- Cooling water systems.
- Fish hatcheries and farms.

Table 21 shows the effectiveness of the various AOPs for the removal of COD. Advanced oxidation processes can be used to solve a number of difficult environmental problems not readily solved by any other method. One such problem is 1,4-Dioxane. This solvent was widely used in industry and has accumulated in groundwater. Ozone/peroxide based AOPs have been successfully applied to treat the groundwater to safe levels permitting it to be used for applications such as drinking water. Another example is methyl tertiary butyl ether (MTBE), a gasoline additive. Leaks of gasoline have contaminated ground water with MTBE around the USA. While the compound can be treated with simple oxidants like ozone alone, the by-products can be more toxic than the MTBE. Advanced oxidation processes can be used to break down the MTBE to safe compounds that require no further treatment. Advanced oxidation processes have also been used to treat by-products of pharmaceutical and personal care products, algal toxins such as microcystin, pesticides and herbicides, and chlorinated hydrocarbons such as trichloroethylene (TCE) and perchloroethylene (PCE).

Table 21 – Removal of COD

Process	H ₂ O ₂ /O ₃ /Catalyst	O ₃ /UV/Catalyst	H ₂ O ₂ /O ₃ /UV/Catalyst
COD removal	30%	49%	59%
Total COD removal	36 g/L	60 g/L	70 g/L

4.11.2 Disinfectant demand

An IWA Publishing book edited by Parsons (2004) reports on a study evaluating the possible microbicidal, and particularly virucidal, efficacy of AOPs. The investigations were performed at a pilot plant installed for the elimination of perchloroethylene from polluted groundwater (reduction efficacy for perchloroethylene from 26 µg/L to 5 µg/L). To enable a reliable evaluation of the microbicidal effect, a set of alternate test organisms was used. As model viruses, bacteriophages MS2 (F+ specific, single-stranded RNA), phiX174 (single-stranded DNA) and PRD-1 (coated, double-stranded DNA) were used while spores of *Bacillus subtilis* were included as possible surrogates for protozoa, and *E. coli* as representatives for traditional indicator bacteria used in water analysis. The microbicidal efficiency was compared to the inactivation by means of ozone under two standard conditions (20°C): (a) 0.4 mg/L residual after 4 min and (b) 0.1 mg/L residual after 10 min. Surprisingly, a good microbicidal effect of the ozone/hydrogen peroxide process was found. This was somewhat unexpected, because it was assumed that the disinfection potential of ozone would have been interfered with by the presence of hydrogen peroxide. *Escherichia coli* and the three test viruses revealed a reduction of about 6-log. In contrast, spores of *Bacillus subtilis* showed after the total process a reduction of 0.4-log. These results matched the effect of the ozone treatment (a) with a residual of 0.4 mg/L after 4 min contact time (20°C). The test condition (b) with a residual of 0.1 mg/L ozone after a contact time of 10 min at 20°C gave a higher reduction of the *B. subtilis* spores (1.5-log). The presented study revealed a satisfying microbicidal efficacy of the ozone/hydrogen peroxide process with respect to vegetative bacteria and viruses (bacteriophages). However, it has to be emphasised that intense mixing and sufficient contact time have to be optimised and tested for each individual installation.

4.11.3 Disinfection / oxidation by-products

The hydroxyl radical has a very high oxidation potential and hence, depending on the dosage applied, is able to completely mineralise several organics. If complete mineralisation is not obtained, by-products will remain in the water, but in general these by-products will be less problematic than the initial targeted organic compound. These by-products will also be more bio-degradable and prone to treatment by means of some sort of biological filter.

4.11.4 Selection criteria (see selection chart)

- i) High colour: AOPs will effectively oxidise colour in water.
- ii) Taste and odour: AOPs copper and silver has no effect on the odour or taste.
- iii) High manganese: AOPs can effectively oxidise manganese.
- iv) High iron: AOPs can effectively oxidise iron.
- v) High turbidity: AOPs have no effect on turbidity.
- vi) High algae: AOPs can kill off algae, the effectiveness varying according to the type of algae and water quality.
- vii) High chlorophyll: AOPs can bleach and oxidise chlorophyll-a.
- viii) High DOC: AOPs are very effective in the oxidation of organics.
- ix) High coliforms: AOPs can inactivate bacteria – limited information is available.
- x) High *Cryptosporidium*: AOPs can effectively inactivate *Cryptosporidium*.
- xi) High *Giardia*: AOPs can effectively inactivate *Giardia*.
- xii) High cyanobacteria toxins: AOPs are effective in oxidising and mineralising these toxins.
- xiii) High ammonia: AOPs are not effective for the removal of high levels of ammonia.
- xiv) High COD: AOPs are very effective in the removal of organic material which contributes to high levels of COD.

4.11.5 Environmental effects

The mechanism of ozonation seems to change at high pH values (USEPA, 1999). The relative rate constants for high pH ozonation of pairs of organic compounds were found to be the same as those for reaction of the same compounds with hydroxyl radicals generated from radiolysis of water.

At higher pH values there is, however, an important factor that works against the effectiveness of ozonation processes. Increasing the pH will not necessarily increase the rate of OH radical destruction of a substrate because of enhanced trapping effects. At pH values greater than 10.3, carbonate ion is a more prevalent species than bicarbonate ion, and the rate constant for the reaction of OH with carbonate ion is over twenty times greater than with bicarbonate ion. The benefit of ozonating at high pH values should therefore be weighed against the scavenging effect of the carbonate ion.

All the various environmental effects as discussed under the separate headings for ozone and UV are applicable.

Advantages of Advanced Oxidation Processes

- Rapid reaction rates.
- Small footprint.
- Potential to reduce toxicity and possibly complete mineralisation of organics treated.
- Does not concentrate waste for further treatment with methods such as membranes.
- Does not produce materials that require further treatment such as spent carbon from activated carbon absorption.
- Does not create sludge as with physical chemical or biological processes (wasted biological sludge).
- Non selective pathway allows for the treatment of multiple organics at once.

Disadvantages of Advanced Oxidation Processes

- Capital intensive.
- Complex chemistry must be tailored to specific application.
- For some applications quenching of excess peroxide is required.

4.12 ALTERNATIVE DISINFECTION PROCESSES

Several other disinfection methods are in use, and those methods are briefly mentioned below. The reasons why these methods are employed differ and are applicable to the particular site situation, availability or non-availability of chemicals, cost, remoteness, emergency situation, etc. These methods do not include the use of physical removal of the pathogens by of filtration (filtration techniques are discussed in section 4.14)

Lime softening: The excess lime process of softening kills bacteria. It is not widely used but because of the bactericidal effect of the high pH values incidental to the process, it is occasionally adopted where the raw water is not only hard but also polluted. The high pH results in the formation of a chlorine residual primarily in the form of hypochlorite (OCI) when the water is chlorinated. The hypochlorite residual has considerably less disinfecting power than hypochlorous acid (HOCl), which exists at lower pH values (USEPA, 1999).

In the lime-softening process, the pH of the water being treated is raised sufficiently to precipitate calcium carbonate and, if necessary, magnesium hydroxide. The normal pH of water is between 6.5 and 8.5. In small systems, lime softening is typically practiced by adding hydrated lime to raw water to raise the pH to approximately 10. This removes calcium carbonate, essentially limestone. If magnesium removal is also required, the pH during softening needs to be closer to 11.

The benefits of softening include the following:

- Reducing dissolved minerals and scale forming tendencies.
- Reducing consumption of household cleaning agents.
- Removing radium 226 and 228.
- Removing arsenic and uranium.
- Removing heavy metals.
- Supplementing disinfection and reducing algal growths in basins.
- Removing certain organic compounds and reducing TOC.
- Removing silica and fluoride.
- Removing iron and manganese.
- Reducing turbidity of surface waters in conjunction with the hardness precipitation process.
- Increasing the Langelier Saturation Index, useful for corrosion control.
- Possibly removes *Giardia Lamblia* cysts.

Solar water disinfection: The germicidal action of sunlight has long been recognised, but the ecological implications and the potentials for practical applications have to be researched more thoroughly. Studies undertaken since 1979 at the American University of Beirut were aimed at solar disinfection of drinking water and oral rehydration solutions based on a batch system using clear or blue-tinted containers made of glass or plastic (USEPA, 1999). The results confirm the effectiveness and feasibility of the solar decontamination of water in small quantities (<3 litres).

Bromine and its compounds have found acceptance as disinfection and sanitising agents in swimming pools and potable water (USEPA, 1999). Some bromine-containing compounds are safer

to use than the analogous chlorine compounds due to certain persistent residuals found in the chlorine-containing materials. Other bromine chemicals are used as a working fluid in gauges, as hydraulic fluids, as chemical intermediates in the manufacture of organic dyes, in storage batteries, and in explosion-suppressant and fire-extinguishing systems. Bromine compounds, because of their density, also find use in the gradation of coal and other minerals where separations are effected by density gradients. The versatility of bromine compounds is illustrated by the commercial use of over 100 compounds that contain bromine. Bromine has been widely used to disinfect swimming pools through the addition of solid bromine releasing agents such as N-bromo-N-chloro-5,5-dimethylhydantoin or dibromocyanuric acid. In South Africa, bromination has been practised at the Kloof gold mine where the high ammonia values in process water exert a high chlorine demand which renders this mode of disinfection uneconomical. Bromine, however, does not react with the ammonia and hence the biocidal properties are available for disinfection.

Iodine has been used as a disinfectant for small drinking water supplies; however, like bromine it is costly to use on a municipal scale. It is not recommended for regular use as a disinfectant due to possible health effects associated with long-term consumption. It can, however, be used for emergency water disinfection (USEPA, 1999).

Heat is a traditional emergency disinfectant, and boiling water for a period of at least 3 minutes will kill most pathogens (USEPA, 1999).

Lemon or lime juice: If lemon/lime juice is available, it is an alternative method of disinfection (WHO, 2004).

4.13 SECONDARY DISINFECTION PROCESSES

The Surface Water Treatment Rule (SWTR) was promulgated in 1989 to provide public health protection against pathogens in surface water supplies across the US. This regulation includes combined filter effluent turbidity standards, requires minimum levels of removal and/or inactivation for viruses (4-log) and *Giardia* (3-log), and mandates filtration for all surface water systems unless strict source water controls are met. The Interim Enhanced Surface Water Treatment Rule (IESWTR), promulgated in December 1998, establishes more stringent filtered water quality standards for turbidity and sets a Maximum Contaminant Level Goal (MCLG) of zero for *Cryptosporidium* for large systems (i.e. those serving more than 10 000 persons) utilising filtration. The Long Term 1 ESWTR (LT1ESWTR) extends the requirements of the IESWTR to smaller systems (serving fewer than ten thousand persons).

In September 2000, the Long Term 2 ESWTR (LT2ESWTR) Agreement in Principle was signed by the EPA and members of the Microbial-Disinfection By-products (M-DBP) Rule Cluster Federal Advisory Committee Act (FACA) Committee (65 FR 83015). The LT2ESWTR agreement includes source water quality-based requirements for up to 2.5-log inactivation and/or removal of *Cryptosporidium* beyond conventional treatment.

Conventional treatment has been proven effective for surface water treatment, and relies on the combination of coagulation, sedimentation, and filtration processes to remove microbial contaminants through a variety of mechanisms. These are also barrier technologies that achieve very high levels of pathogen removal primarily through a sieving or size exclusion mechanism. Microfiltration (MF) and Ultrafiltration (UF) are two technologies that have consistently proven effective for the removal of larger pathogens such as *Giardia* and *Cryptosporidium*. The SWTR addresses conventional treatment plants as well as other media filtration technologies such as direct filtration, slow sand filtration, and diatomaceous earth filtration.

The efficacy of water treatment methods is widely measured using the log removal value (LRV) as calculated in Equation [46].

$$\text{LRV} = \log_{10} (C_{\text{in}} / C_{\text{out}}) \quad [46]$$

Where C_{in} is influent pathogen concentration and C_{out} is effluent pathogen concentration. Hence, for a given pathogen, LRV 2 reflects 99% removal, whilst LRV 4 reflects 99.99% removal (USEPA, 1999).

Conventionally, pre-treatment via coarse filters (e.g. gravel, sand) reduces gross turbidity (pathogen populations are typically associated with particles), being especially effective in reducing algae and protozoa concentrations (LRV 2 to 3 is readily achievable). Simple settlement in storage reservoirs or through bank filtration can also provide primary pathogen removal. Storage not only permits settlement, but also allows time for bacterial and viral death outside the host environment. However, such simple treatment systems are rarely sufficient in themselves to meet the high pathogen removal standards required for effective health protection.

Pre-treatment is often supplemented with enhanced clarification treatment by means of flocculation or coagulation and subsequent sedimentation. Optimised systems can achieve LRV 1 to 2 for viruses, bacteria and protozoa. Higher LRVs for major pathogen groups are generally achieved using high-rate clarifiers, although due care is required in problem areas with alga removal, so as not to disrupt algal cells and allow toxin release. Dissolved air flotation is a suitable alternative for the removal of algae (LRV 1 to 2 for many species), and is also an effective approach for *Cryptosporidium* oocyst removal (LRV 2 to 2.6). Gravel and slow sand filtration may be the only cost-effective technologies to achieve pathogen removal in some circumstances. Depending upon flow rates, media size and uniformity, and filter bed depth, these systems can be very effective. Wide-ranging LRVs of up to 5 have been reported in tests, whilst operational experience in the USA demonstrates total coliform LRV up to 2.3 and very effective *Giardia* removal (LRV ca. 4) by sand filters, particularly after the establishment of microbiological films on the media. However, treatment capacities can be low and pathogen removal efficiencies can be highly variable; *Cryptosporidium* removal in particular has generally been shown to be relatively poor (LRV often 0.5) (USEPA, 1999).

Membrane filtration has become widespread both in new-build water treatment plants and as a retrofitment to existing plants. Membrane filtration has grown in prominence as a viable wastewater treatment approach over the last decade as technology developments have improved membrane durability, system reliability and cost-effectiveness. In many cases the primary objective of a membrane filtration system is to remove suspended solids and COD to meet stringent discharge consents. The size exclusion capability of MF and UF membranes shows the potential for concurrent pathogen removal. Microfiltration removes algae, protozoa and many bacteria effectively (e.g. LRV between 4 and 7 for *Giardia* and *Cryptosporidium* using a 0.1 μm membrane).

Virus removal by MF is poor, although it can be better than anticipated from simple pore-size considerations if virus species are strongly associated with particles. Accordingly, for effective virus removal UF is normally required. Virus removal by UF is more efficient with lower molecular weight cut-off membranes, as the key removal mechanism is physical exclusion (the influence of microfilm composition is secondary). Importantly, pathogen removal efficiency is independent of influent quality and other operating parameters, typically being in the range LRV 4 to 7 for the key pathogens.

Membrane filtration using UF can effectively remove pathogens to the very high degree achieved by chemical oxidative disinfection, and is without the associated problems and costs of storing and using corrosive agents. However, significant problems arise should membrane integrity fail (fibres tear, membrane is scratched, etc.) as pathogen removal efficiency can dramatically deteriorate. The development of robust membrane materials overcomes this issue, but effective effluent monitoring to

identify integrity problems remains an essential component of a MF/UF treatment system. Direct (e.g. pressure testing) or indirect (e.g. particle monitoring) integrity testing approaches have been successfully used. For potable water supply, post-membrane disinfection remains necessary to achieve secondary disinfection. In high-quality supply applications, nanofiltration (NF) or reverse osmosis (RO) together with UV disinfection is well established. Normally, MF/UF pre-treatment is used, with oxidative disinfection commonly employed to restrict biofilm establishment on the NF/RO membrane. Ultraviolet-B or UV-C light is best for pathogen inactivation (200-310 nm) with doses of around 30 mWs/cm² suitable for all but the most resilient of viruses.

CHAPTER 5 - OXIDATION AND DISINFECTION TECHNOLOGY

- 5.1 - Introduction
- 5.2 - Oxidant and disinfectant generation technology
- 5.3 - Oxidant and disinfectant storage
- 5.4 - Oxidant and disinfectant dosing and mixing technology
- 5.5 - Oxidant and disinfectant process reactor technology
- 5.6 - Oxidant and disinfectant dosing maintenance

5.1 INTRODUCTION

Chapter 4 dealt with the selection of oxidation and disinfection processes available to meet the treatment objectives. The next step is to select the most appropriate process technology. The selection and design of appropriate technology is influenced by site-specific conditions and should be undertaken with the necessary professional and technical guidance including pilot plant work and detail engineering. This chapter describes the variety of oxidation and disinfection technology as follows:

- The **generation** of oxidants and disinfectants will be discussed first. A distinction will be made between oxidants that are generated on-site and those that are generated off-site.
- For those oxidants that are generated off-site, **storage** facilities need to be provided.
- Oxidants need to be mixed with the main process stream in order to achieve the desired effect. Various types of **dosing and mixing** equipment are available and will be discussed.
- Oxidants and disinfectants also require **reaction vessels** that support the reaction type and contact time. Disinfection reactors need to be hydraulically efficient and meet minimum CT requirements.
- Finally, consideration should be given to the **maintenance** aspects of oxidation and disinfection equipment.

5.2 OXIDANT AND DISINFECTANT GENERATION TECHNOLOGY

The oxidant and disinfectant generation technology is sub-divided into on-site and off-site generation technology. The choice is largely dictated by the size of the plant considered and unique economics applicable to each plant.

5.2.1 On-site generation technology

It is not possible, and in some cases not safe, to generate some oxidants and disinfectants on-site. The technology for on-site generation is limited to the processes using air or oxygen and some chlorine based products.

5.2.1.1 Sodium hypochlorite generation

Dilute sodium hypochlorite solutions can be generated electrochemically on-site from a brine solution. Generally, the commercial or industrial grade solutions produced have hypochlorite strengths of 10 to 16%. The stability of sodium hypochlorite solution depends on the hypochlorite concentration, the storage temperature, the length of storage (time), the impurities of the solution, and exposure to light. Decomposition of hypochlorite over time can affect the feed rate and dosage, as well as produce undesirable by-products such as chlorite ions or chlorate. Because of the safety concerns related to

chlorine gas many users are investigating on-site generation of hypochlorite in lieu of chlorine gas. The sodium hypochlorite solution needs to be stored on-site for subsequent dosing.

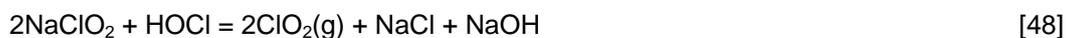
5.2.1.2 Chlorine dioxide generation

Chlorine dioxide cannot be compressed or stored commercially as a gas because it is explosive under pressure. Therefore, it is never shipped, but generated on site. A number of generating technologies is available and the differences are primarily related to the raw products used in its manufacture. Most commercial generators use sodium chlorite (NaClO_2) as the common feedstock chemical to generate chlorine dioxide for drinking water application. Recently, production of chlorine dioxide from sodium chlorate (NaClO_3) has been introduced as a generation method wherein NaClO_3 is reduced by a mixture of concentrated hydrogen peroxide (H_2O_2) and concentrated sulphuric acid (H_2SO_4).

Some newer generators produce a continuous supply of dilute gaseous chlorine dioxide in the range of 10 to 40 kPa (abs) rather than in an aqueous solution. For potable water treatment processes, aqueous solutions between 0.1 and 0.5% are common from a number of current generation technologies (USEPA, 1999).

For potable water applications, chlorine dioxide is generated from sodium chlorite solutions. The principal generation reactions that occur in the majority of generators have been known for a long time. Chlorine dioxide can be formed by sodium chlorite reacting with gaseous chlorine (Cl_2), hypochlorous acid (HOCl), or hydrochloric acid (HCl).

The reactions are:



Conventional systems employ sodium chlorite with either acid, aqueous chlorine, or gaseous chlorine. Emergent technologies include electrochemical systems, a solid chlorite inert matrix (flow-through gaseous chlorine) and a chlorate-based emerging technology that uses concentrated hydrogen peroxide and sulphuric acid.

The conventional chlorine-chlorite solution method generates chlorine dioxide in a two-step process. First, chlorine gas is reacted with water to form hypochlorous acid and hydrochloric acid. In the second step, these acids then react with sodium chlorite to form chlorine dioxide. The ratio of sodium chlorite to hypochlorous acid should be carefully controlled.

Acid-chlorite solution: Chlorine dioxide can be generated by acidification of a sodium chlorite solution using hydrochloric acid according to the reaction described in Equation [50].

Aqueous chlorine-chlorite solution: Chlorite ion reacts with hydrochloric acid and hypochlorous acid to form chlorine dioxide, commonly referred to as conventional systems. If chlorine gas and chlorite ion are allowed to react under ideal conditions, the resulting pH of the effluent may be close to 7. To fully utilise sodium chlorite solution, the more expensive of the two ingredients, excess chlorine, is often used. This approach lowers the pH and drives the reaction further towards completion. The reaction is faster than the acid-chlorite solution method, but much slower than the other commercial methods described in the following discussion.

Recycled aqueous chlorine: In this process aqueous chlorine and chlorine gas are injected into a continuously circulating water loop. This eliminates the need for a great excess of Cl₂ gas to be fed to the generator since the molecular chlorine will dissolve in the feed water, and thus maintain a low pH level of the feed water. Loop-based generators keep chlorine at or above saturation levels. The low pH condition results in high yields of chlorine dioxide of greater than 95%.

Gaseous chlorine-chlorite solution: Sodium chlorite solution can be vaporised and reacted under vacuum with molecular gaseous chlorine. The acid-sodium hypochlorite-sodium chlorite method of generating chlorine dioxide is used when chlorine gas is not available. First, sodium hypochlorite is combined with hydrochloric or another acid to form hypochlorous acid. Sodium chlorite is then added to this reaction mixture to produce chlorine dioxide.

5.2.1.3 Chloramines

Chloramines are generated on-site, and the most tried and tested technology for the generation of chloramines involves the addition of ammonia to a diluted chlorine solution. (The generation and storage of chlorine is described later in the section.)

Ammonia is dosed either as a concentrated (25%) ammonium hydroxide (NaOH) solution or injected as anhydrous ammonia gas. The use of ammonium hydroxide is the most simple and reliable method of dosing ammonia.

In the case of dosing ammonia gas, two types can be considered. One system dissolves ammonia gas under pressure and another system dissolves ammonia via a vacuum eductor system. In the case of the latter, particular attention should be paid to the quality of the water at the point of injecting the gas. Softened water with a hardness of less than 30 mg/L as CaCO₃ is required for the carrier stream. Otherwise, the ammonia addition will precipitate scale that will plug the eductor and application point. In high alkalinity water it has been found that the dosing points scale up in a short time due to the formation of ammonium carbonate crystals. Ammonia gas should in such cases preferably be first dissolved and then mixed into the main process. Various cleaning methods have been proposed to clean the blocked nozzles, but with limited success.

The cost of transporting the ammonium hydroxide, which contains at least 75% water, compared to ammonia gas will be one of the parameters used in deciding the most cost effective approach. The other key parameter will be the simplicity of the operation and the control. Dosing liquid at a controlled rate is often much simpler and reliable than dosing and mixing a compressible gas such as ammonia into a process stream. Unless the operating costs of an ammonia gas dosing installation are significantly less compared to ammonium hydroxide, it is not recommended for small to medium sized water treatment plants. Ammonium hydroxide is stored in steel or glass fibre reinforced plastic (GRP) tanks and needs to be supplied with a liquid trap to limit the evaporation of ammonia from the tank.

The ammonia should be dosed in a ratio of 4:1 to 5:1 and adjusted to limit the free ammonia and prevent the formation of di- and tri-chloramines.

5.2.1.4 Oxygen

Oxygen is used as an oxidant for iron and manganese oxidation and also as a raw product for the generation of ozone (discussed below). Oxygen can be made on-site on a small scale by the use of oxygen concentrating technology. Pressure swing adsorption is a process whereby a special molecular sieve is used under pressure to selectively remove nitrogen, carbon dioxide, water vapour and hydrocarbons from air, producing an oxygen rich (80-95% O₂) feed gas. The components used in PSA systems are similar to high pressure air feed systems in that both use pressure swing molecular

absorption equipment. The economic size of PSA units has reduced significantly during the past decade. This has made the on-site generation of oxygen for small scale WTW feasible.

Cryogenic oxygen generation: A process that cools, dehydrates, compresses and cleans air to form LOX. It should be noted that this type of oxygen generation will only be applicable for a plant with a very large oxygen demand. In most cases, it would be more cost effective to source LOX from a nearby oxygen plant.

5.2.1.5 Ozone

Because ozone is an unstable molecule, it should be generated at the point of application for use in water treatment. It is generally formed by combining an oxygen atom with an oxygen molecule as in Equation [50].



This reaction is endothermic and requires a considerable input of energy.

Most commercially available ozone generators generate ozone by means of the corona discharge process. This process involves the circulation of air or oxygen past an electrode charged with a high voltage. The discharge of the high voltage between the electrode nodes is responsible for the generation of ozone.

Ozone generation using oxygen is more energy efficient compared to ozone generated by means of air. The two key cost drivers for ozone generation is the cost of producing the oxygen source and the cost of the energy in producing the ozone.

In the case of an oxygen source the ozone generation operating cost comprises the LOX and the electricity cost. In the case of an air source, the operating cost includes the cleaning and drying of the air and the electricity cost of a much larger and more inefficient ozone generator as well as the air handling equipment.

In some cases, depending on the cost of energy and LOX, it may still be more cost effective to consider an air supplied ozone generator. It should, however, be kept in mind that an ozone generation system, using an air or PSA oxygen source will require significantly more maintenance (in the order of 15% of the original purchase cost per annum) and will complicate the operation significantly.

One of the key decisions that need to be made when selecting on-site ozone generation is therefore the source of the oxygen. A comprehensive cost-benefit analysis is required to assess all operational and life cycle cost aspects.

Once the oxygen source is selected, the type of ozone generator needs to be selected. The key decisions that need to be taken in selecting the appropriate ozone generation equipment include:

- Size and number of ozone generators.⁶
- Oxygen source.

⁶ The size of the ozone installation is the most important design decision that needs to be made and it is therefore essential that this decision is based on site specific empirical evidence. A pilot study that establishes the ozone demand, decay, disinfection and oxidation rates is therefore an essential step. The use of typical ozone dosing rates is not recommended as each water source has particular aspects that leads to a unique ozone demand.

- Unit energy use.
- Unit LOX/air use.
- Reliability.
- Maintenance.
- Supportability.
- Skills requirements.

Finally, it should be noted that an ozonation system adds a new level of complexity to a water treatment plant. Skilled operators and maintenance personnel will be required to operate and maintain an ozone plant. In addition, an ozone plant should be monitored and controlled continuously in order to optimise production costs. Two ozone plants producing the same amount of ozone can have operating costs that differ by as much as 200%. Non-optimal ozone generation will have significant long term financial implications.

5.2.1.6 Peroxone

Peroxone is generated on-site by adding hydrogen peroxide to a dilute ozone solution. Hydrogen peroxide is generated off-site and stored in bulk tanks. The peroxone process also requires an ozone generation system as described above. The process involves two essential steps: ozone dissolution and hydrogen peroxide addition. Hydrogen peroxide can be added after ozone (thus allowing ozone oxidation and disinfection to occur first) or before ozone (i.e. using peroxide as a pre-oxidant, followed by hydroxyl radical reactions), or simultaneously. Addition of hydrogen peroxide following ozone is the best way to operate; however, a system cannot obtain a CT credit unless the ozone residual is sufficiently high. It is therefore more efficient to add ozone first to obtain CT disinfection credit, followed by peroxide for hydroxyl radical oxidation. In practice, the addition of hydrogen peroxide to the second stage of ozonation can be achieved by injecting the hydrogen peroxide into the last chamber of an ozone contactor. The most efficient operation is to use ozone first to obtain CT credit and peroxone second for micropollutant destruction. Energy consumption of the peroxone process includes that for ozone generation and application, plus for metering pumps to feed peroxide. The peroxide addition step does not require any more training from an operator than any other liquid chemical feed system. Systems should be checked daily for proper operation and for leaks. Storage volumes should also be checked daily to ensure sufficient peroxide is on hand, and to monitor usage.

The performance of peroxone is dependent on the peroxide:ozone ratio. Studies reported by USEPA (1999) suggested that the optimal ratio for disinfection was ≤ 0.3 . A study by van der Walt (1997) investigated the benefits of using peroxone.

The peroxide metering pumps should be housed with adequate space around each pump for maintenance access. These pumps are generally not very large, so space requirements are not significant. Secondary containment should be provided.

5.2.1.7 Ultraviolet radiation

Ultraviolet radiation is generated on-site by exposing treated water to an array of UV lamps. Various different configurations are available and UV lamps are available from a number of suppliers. The effectiveness of the UV equipment is dependent on the clarity (transmissivity) of the water. Ultraviolet can penetrate more deeply if the water is clearer. The key parameters that dictate the selection of the equipment include:

- Target pathogens and associated radiation dose.

- Plant flow rates.
- Size and number of units.
- Water quality (transmissivity, turbidity and colour).
- Presence of scale and biofilm forming compounds.
- Self cleaning equipment (wipers) effectiveness, life and cost.
- Lamp and quartz sleeve robustness, life and replacement cost.
- Equipment reliability.
- Maintenance (cost of tubes).

Producing UV radiation requires electricity to power UV lamps. The lamps typically used in UV disinfection consist of a quartz tube filled with an inert gas, such as argon, and small quantities of mercury. Ballasts control the power to the lamps. Ultraviolet lamps operate in much the same way as fluorescent lamps – UV radiation is emitted from electron flow through ionised mercury vapour to produce UV energy in most units. The difference between the two lamps is that the fluorescent lamp bulb is coated with phosphorus, which converts the UV radiation to visible light. The UV lamp is not coated, so it transmits the UV radiation generated by the arc. Both LP and MP lamps are available for disinfection. Low pressure lamps emit their maximum energy output at a wavelength of 253.7 nm, while MP lamps emit energy with wavelengths ranging from 180 to 1370 nm. The intensity of MP lamps is much greater than LP lamps. Thus, fewer MP lamps are required for an equivalent dosage. For small systems, the MP system may consist of a single lamp. Although both types of lamps work equally well for inactivation of organisms, LP UV lamps are recommended for small systems.

Most conventional UV reactors are available in two types; namely, closed vessel and open channel. For drinking water applications, the closed vessel is generally the preferred UV reactor due to its smaller footprint, minimised pollution from airborne material, and minimal personnel exposure to UV.

The hydrodynamic behaviour of a closed vessel UV reactor should be carefully considered. Water passing through the UV vessel should receive equal radiation and residence time and should exhibit plug flow characteristics with as little as possible back mixing. Computational fluid dynamics have been used in a number of cases to improve the hydrodynamic efficiency of UV vessels.

5.2.2 Off-site generation technology

5.2.2.1 Chlorine gas

Chlorine gas is only generated at large off-site installations associated with the chlor-alkali industry. Chlorine gas can be generated by a number of processes including the electrolysis of alkaline brine or hydrochloric acid, the reaction between sodium chloride and nitric acid, or the oxidation of hydrochloric acid. Most of the chlorine produced in South Africa is manufactured from the electrolysis of brine and caustic solutions. Once produced, chlorine is packaged as a liquefied gas under pressure for delivery to site in cylinders. In South Africa, chlorine gas is supplied in small (68 kg) and large (1000 kg) gas cylinders and transported to users.

5.2.2.2 Calcium hypochlorite

To produce calcium hypochlorite, hypochlorous acid is made by adding chlorine monoxide to water and then neutralising it with lime slurry to create a solution of calcium hypochlorite. The water is removed from the solution, leaving granulated calcium hypochlorite. Generally, the final product contains up to 70% available chlorine and 4-6% lime.

5.2.2.3 Potassium permanganate

Potassium permanganate is only supplied in dry form. The solubility of KMnO_4 in water is 6.4 g/mL at 20°C. Potassium permanganate is typically supplied in buckets or drums and supplied in various grades. Pure KMnO_4 is non-hygroscopic but technical grades will absorb some moisture and will have a tendency to cake together. For systems using dry chemical feeders, a free-flowing grade is available that contains anti-caking additives.

5.2.2.4 Copper, silver and calcium

Copper, silver and calcium salts are generally not generated on-site. Copper is purchased from suppliers in powder or crystal form. It is often used as a disinfectant or biocide for the control of algae in impoundments and swimming pools.

Silver is not often sold in large quantities for water treatment purposes, but only in pre-prepared or pre-packed form for point of use type water treatment devices. Silver is often found in the form of silver impregnated activated carbon found in home treatment devices.

Calcium as used in a high lime process is used in large quantities and can be supplied in the form of slaked lime, quick lime or limestone. Water can be mixed directly with $\text{Ca}(\text{OH})_2$ for pH adjustment and coagulation purposes. The pH adjustment is often required to assist in the subsequent oxidation process. The disinfection qualities are not directly as a result of the calcium, but as a result of the elevated (and lethal to some organisms) pH.

5.2.2.5 Peroxone

Hydrogen peroxide, used in the peroxone process is not generated on-site due to safety considerations. Hydrogen peroxide is purchased from chemical suppliers and is commercially available in 35, 50, and 75% strengths (liquid). Peroxide is supplied in drums or by tanker. Price depends on strength and quantity.

5.3 OXIDANT AND DISINFECTANT STORAGE

The on-site generated oxidants and disinfectants are generally not stored on-site, but applied as and when needed. This section will therefore only discuss the storage requirements for on-site generated oxidants.

5.3.1 Chlorine

Chlorine gas is stored and transported to the treatment plant in steel cylinders. In South Africa, the most common chlorine cylinder sizes are 68 kg or 1 ton cylinders. In exceptional cases larger bulk installations can be arranged. Each cylinder has two valves; one valve is connected to the upper part of the cylinder which draws from the vaporised chlorine gas, and the second valve is connected to the liquid chlorine in the cylinder. Operators should ensure that the chlorine dosing equipment is connected to the correct valve.

Due to the cooling effect of vaporising chlorine, cylinders can only supply a maximum of about 6-7 kg/hr chlorine gas. Chlorine dosing rates in excess of these will require the installation of more than one cylinder installed in parallel or the installation of heated chlorine vaporisers.

5.3.2 Sodium hypochlorite

Sodium hypochlorite is delivered in pre-packed plastic containers of various sizes. Bulk deliveries can also be arranged in storage tanks on-site. Polyethylene tanks are suitable for storing sodium hypochlorite.

5.3.3 Chloramines

Ammonia gas is stored in cylinders similar to chlorine. In cases where ammonium hydroxide is used, polyethylene or rubber lined steel tanks can be used. It is essential to make provision for properly ventilated loading facilities and pressure release valves on ammonium hydroxide tanks.

5.3.4 Calcium hypochlorite

Calcium hypochlorite is sold in dry powder, flake or pellet form. Various container sizes are available from 0.5 to >210 L containers. The choice of granules, flakes or pellets depends on the dosing requirements. Calcium hypochlorite should be stored in a well ventilated place not close to any equipment that can be impacted by chlorine fumes such as electric panels or exposed metal surfaces.

5.3.5 Oxygen/ozone

Liquid oxygen is stored in cylinders of various sizes ranging from a few kilograms to several tons. Large installations comprise cryogenic cylinders with all the necessary safety devices and evaporating equipment to ensure that the LOX is completely vaporised. Local gas suppliers should be contacted for detailed installation requirements.

5.3.6 Potassium permanganate

A concentrated KMnO_4 solution (typically 1 to 4%) is prepared on-site for water treatment applications; the solution is pink or purple in colour.

Depending on the amount of permanganate required, these solutions can be made up in batch modes, using dissolver/storage tanks with mixers and a metering pump for small feed systems. Larger systems will include a dry chemical feeder, storage hopper and dust collector configured to automatically supply permanganate to the solution dissolver/storage tank. Potassium permanganate solution is made up of dry crystalline permanganate solids added to make-up water and then stirred to obtain the desired permanganate concentration. Potassium permanganate is a strong oxidiser and should be carefully handled when preparing the feed solution. No by-products are generated from making the solution.

5.3.7 Peroxide

Peroxide is a strong oxidant and personnel should avoid contact with the product. Secondary containment should be provided for storage tanks to contain any spills. Storage containers may explode in the presence of extreme heat or fire. The storage area can range from small, where peroxide is obtained in drums, to large storage tanks. Peroxide has a lower freezing point than water. Housing or heat tracing should be provided for storage tanks and exterior piping if extended periods with temperatures below freezing are anticipated. Peroxide can be stored in polyethylene drums or tanks. The specific gravity for a 50% solution is 1.39 which should be considered in the design of the tank walls. Even when stored correctly peroxide deteriorates gradually over time, and can do so rapidly if contaminated with heat or exposure to certain materials.

5.4 OXIDANT AND DISINFECTANT DOSING AND MIXING TECHNOLOGY

5.4.1 Gas injection systems

5.4.1.1 Chlorine, ammonia and ozone vacuum gas injection systems

Chlorine gas injection: The most common technology to dose chlorine gas is via vacuum injection. This technology incorporates a motive water system that creates a vacuum by means of a venturi. The low pressure throat of the venturi is connected to a vacuum regulator that creates sufficient vacuum to draw chlorine gas from the chlorine gas feeder. The gas feeder comprises a rotameter calibrated for chlorine gas and a control valve to adjust the chlorine gas feed rate to the injector. The vacuum regulator ensures that a constant vacuum is maintained when the gas feed rate is adjusted. Chlorine is highly soluble in water and the chlorine injected is rapidly dissolved into the motive water stream. Several manufacturers supply a variety of different sizes from as little as a few grams per hour up to more than 100 kg/hr.

It is important to establish the maximum chlorine gas draw-off rate from the cylinder in use. As chlorine is withdrawn from a cylinder the vapour expands and cools the cylinder down. Excessive draw-off rates can cause the cylinder to freeze, especially during winter. Should the required draw-off rate be higher than the available draw-off rate two options can be considered. Larger, or more, cylinders can be connected to a manifold of cylinders connected in parallel. Alternatively, an approach often implemented in larger installations is to draw chlorine liquid from the cylinders into a specially heated chlorine vaporiser. Much higher draw-off rates can be achieved using vaporisers. Safety measures need to be put in place to ensure that the pipe manifold is heated all the time and that chlorine liquid cannot enter the chlorine feed equipment.

Ammonia gas injection: Ammonia gas dosing is implemented in a similar way to chlorine gas. Additional care needs to be taken with regard to the motive water as hard water will form ammonium carbonate crystals and will block injectors and dosing points in a very short time.

Ozone gas injection: Ozone is less soluble in water compared to chlorine and even oxygen. Much larger volumes of water are therefore required to dissolve ozone in water. Ozone can also be introduced into water based on the same principle as used for chlorine injection. A number of additional measures are, however, required to deal with the large quantities of gas.

Ozone gas injection comprises a set of recycle pumps that takes a portion of the water from the main process stream (also referred to as a sidestream) and push it through large venturi type injectors and static mixers that ensure that the injected ozone gas is well mixed with the sidestream. The ozone gas and water mixture is then reintroduced into the main process stream, either through nozzles or a static mixer in the main process pipeline. In order to separate the large quantities of gas from the sidestream before it is reintroduced into the main process, degassing vessels are often employed.

The injection rate can be controlled by the recycle pump flow rate as well as the ozone gas generator production rate. A mass flow controller is often installed to ensure that a set ozone dose is applied to the main process stream.

A key parameter that should be considered is the gas to liquid ratio. This ratio should be less than 1 part gas to 10 parts water, but will vary depending on the supplier. Meeting this criterion typically requires high ozone concentration (~10%) and low ozone dosing rates. To meet the CT disinfection requirements, additional contact time is required after the injector, typically in a plug flow reactor. The

additional contact volume is determined in conjunction with the applied ozone dosage and estimated residual ozone concentration to satisfy the disinfection CT requirement. Figure 10 illustrates a process flow diagram for a typical sidestream injection system.

5.4.1.2 Oxygen and ozone pressurised gas injection systems

Oxygen and ozone are often injected under pressure in order to improve the transfer efficiency. Apart from the sidestream injection systems three other types of ozone injection system are available; bubble diffuser systems, deep U-tube systems and turbine mixer systems. Each of these systems will briefly be discussed.

Bubble diffuser systems: The bubble diffuser contactor is the most common ozone contacting system throughout the world. This method offers the advantages of no additional energy requirements, high ozone transfer rates, process flexibility, operational simplicity, and no moving parts (USEPA, 1999). Figure 10 shows a process flow diagram of a three stage ozone bubble diffuser contactor. This illustration shows a counter-current flow configuration (ozone and water flowing in opposite directions). The number of contacting stages varies depending on the treatment objectives, and can vary from two to more than ten. Bubble diffuser contactors are typically constructed with 6 meter water depths to achieve ozone transfer efficiency between 85 and 95%.

Bubble diffuser contactors use ceramic or stainless steel diffusers that are either rod-type or disc-type to generate bubbles of 2 to 4 mm. Design considerations for these diffusers include the gas flow rate per diffuser, the diffuser spacing and the headlosses in the piping system from the ozone generator to the diffuser manifold. The configuration of the bubble diffuser contactor structure should best be designed to provide plug flow hydraulics. Channelling of bubbles is dependent on the type of diffusers used and the spacing between diffusers. This configuration will minimise the overall volume of the contactor while still meeting the CT requirements for the system.

Computational fluid dynamics have been used successfully to ensure that plug flow is achieved prior to construction. Contactor volume is determined in conjunction with the applied ozone dosage and estimated residual ozone concentration to satisfy the disinfection CT requirement. Care should be taken to enable diffuser pore maintenance in cases where iron and manganese oxidation is required.

Deep U-tube systems: Deep U-tubes are not used very often due to the cost involved in constructing a large shaft of about 20 m deep in which ozone is dissolved in a co-current mode. There is only one known U-tube ozone installation in South Africa.

Turbine mixer systems: Turbine mixers are used to feed ozone gas into a contactor and mix the ozone with the water in the contactor. Ozone transfer efficiency for turbine mixers can be in excess of 90%. However, the power required to achieve this efficiency is higher than that of bubble diffuser systems. Turbine mixing basins vary in water depth from 2 to 5 m, and dispersion areas vary from 3 to 5 m (USEPA, 1999). The turbine mixer basin may not have sufficient contact time to meet disinfection CT requirements and may have to be supplemented with additional contact basins.

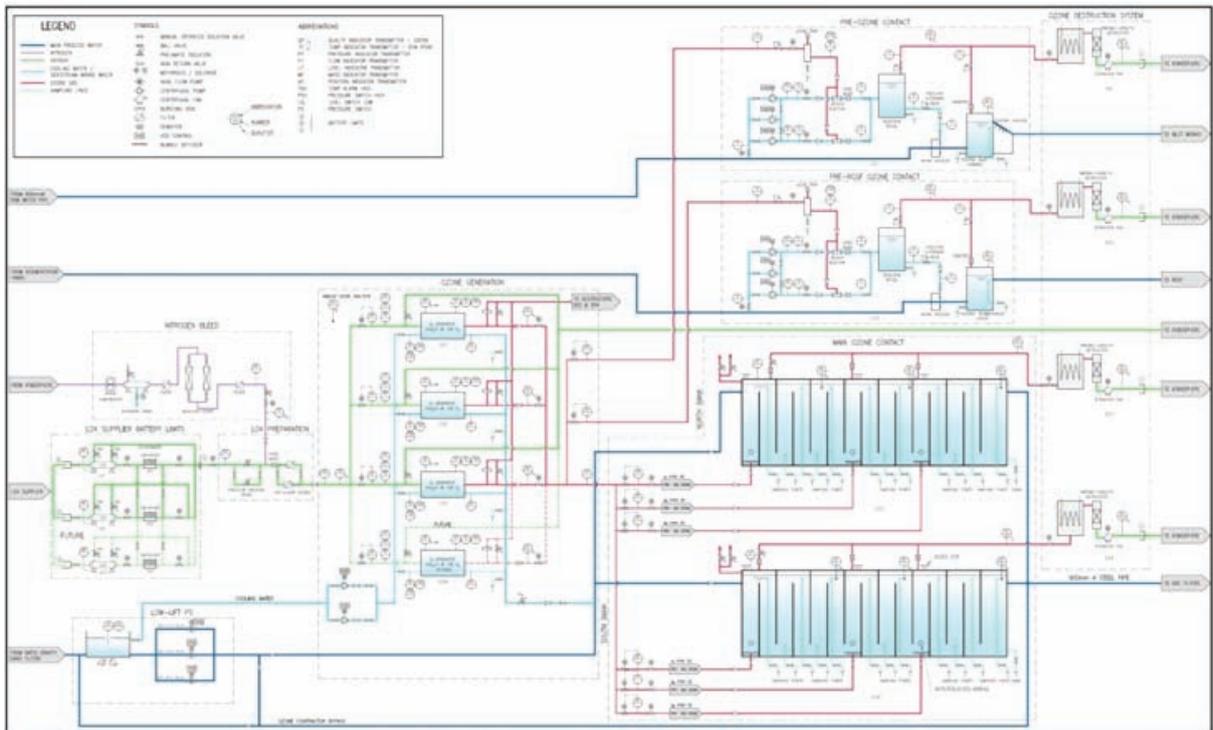


Figure 10 – Schematic flow diagram of ozone sidestream and bubble diffusers

Off-gas systems: Since not all the ozone is transferred into the water, the contactor chambers of all ozone injection systems are covered to contain the off-gas. The concentration of ozone in the off-gas from an ozone contactor is usually well above the fatal limit. For example, at about 90% transfer efficiency, a 10% ozone feed stream will still contain 10 000 ppm of ozone in the off-gas (USEPA, 1999). Off-gas is collected and the ozone converted back to oxygen prior to release to the atmosphere. The off-gas destruct unit is designed to reduce the concentration to 0.1 ppm of ozone by volume, the current limit set by the Occupational Health and Safety Act (1993) for worker exposure in an eight hour shift. A blower is used on the discharge side of the destruct unit to pull the air from the contactor, placing the contactor under a slight vacuum to ensure that no ozone escapes. Ozone is readily destroyed at high temperature (>350°C) or by a catalyst operating above 100°C. Most ozone destruct units employ both heat and catalyst referred to a thermo-catalytic conversion.

5.4.2 Liquid dosing systems

5.4.2.1 Sodium hypochlorite

Sodium hypochlorite solution is typically fed directly into the process water using a dosing pump. Similar to chlorine solution, sodium hypochlorite is mixed with the process water using either a mechanical mixer or an induction mixer. Sodium hypochlorite solution is typically not diluted prior to mixing to reduce scaling problems.

5.4.2.2 Potassium permanganate

Caution should be taken to prevent overdosing, in which case excess manganese will pass through the treatment plant. Proper dosing should be maintained to ensure that all of the permanganate is reduced to Mn precipitate and removed from the plant upstream of, or within, the filters. If residual manganese is reduced downstream of the filters, the resulting solids can turn the finished water a

brown/black colour and precipitate in the homes of consumers on heat exchange surfaces such as hot water heaters and dishwashers.

In general, potassium permanganate does not interfere with other treatment processes or plant conditions. Permanganate can be added downstream of, or concurrently with, coagulant and filter polymer aids. Powdered activated carbon (PAC) and permanganate should not be added concurrently. Powdered activated carbon should be added downstream of permanganate because it may consume permanganate, rendering it unavailable for the oxidation of target organics.

If potassium permanganate is not controlled properly the manganese in the finished water can exceed the regulated SANS 241 level of 0.05 mg/L.

Care should also be taken to maintain filters aerobically to prevent the reducing of Mn to soluble Mn^{2+} which will pass through the filters. Another source of manganese can be the recycled filter backwash water. Overdosing of permanganate in conventional plants is generally corrected by settling the excess MnO_2 solids in the settling basin. Removal of the excess permanganate can be monitored qualitatively by observing the disappearance of the pink colour characteristic of permanganate.

The space requirements for permanganate feed equipment vary depending on the type and size of the feed system. Dry feed systems require about half the floor area of batch systems because batch systems typically have two dissolving tanks for redundancy. However, the head space requirements are greater for dry feed systems where the storage hopper and dust collector are stacked on top of the dry feeder.

It is often convenient to first prepare a stock solution of permanganate and then use diaphragm metering pumps to accurately dose permanganate.

5.4.2.3 Hydrogen peroxide

The metering pumps used to add peroxide should be housed with adequate space around each pump for maintenance access. These pumps are generally not very large, so space requirements are not significant. Peroxide is added to the water with metering pumps to accurately control the dose. Pumps should be designed to prevent potential air binding of peroxide off-gas. Multiple pumps should be provided for redundancy. Acceptable pipe materials for peroxide include 316 stainless steel, polyethylene, chlorinated polyvinyl chloride (CPVC), and Teflon. Gaskets should be Teflon because natural rubber, Hypalon and ethylene propylene diene M-class rubber (EPDM rubber) are not resistant to hydrogen peroxide. Metering pumps' heads should be constructed of peroxide resistant materials.

As with any chemical added to water, adequate mixing should be provided. The point of application of peroxone for disinfection should be after ozonation. Ozone contact should precede addition of hydrogen peroxide. For oxidation, peroxone can be added prior to coagulation/sedimentation or filtration depending on the constituents to be oxidised.

5.4.3 Solid dosing systems

Commercial high-level calcium hypochlorite contains at least 70% available chlorine. Under normal storage conditions, calcium hypochlorite loses some of the available chlorine with time. In South Africa, calcium hypochlorite can be delivered in containers from a few grams to 50 kg and in granular, flake or compressed tablet form. It is not recommended to dose calcium hypochlorite in solids form, but to first prepare a solution by mixing the calcium hypochlorite with a small water feed, just enough

to dissolve the calcium hypochlorite. The concentrated chlorine solution can then be introduced into the process and controlled by various means.

5.5 OXIDANT AND DISINFECTANT PROCESS REACTOR TECHNOLOGY

Any oxidation or disinfection process needs a container or process reactor in which the process takes place. Some processes require a reactor that supports mixing and other processes require plug flow reactors. In most water treatment processes both types of reactors are required.

5.5.1 Mixing tanks

Mixing tanks require rapid dispersion of the substance that is being dosed into the reactor fluid (water). Liquid-liquid mixing tanks often employ mechanical or static mixers to achieve mixing of the disinfectant or oxidant with the main process. Gas-liquid mixing tanks present more of a challenge as the gas does not only have to be dispersed, but conditions also need to be created for its dissolution. Vacuum injectors have been used for many years with success. Injectors have been used for the dispersion of chlorine, ammonia, oxygen and ozone. The injector is designed in such a way that the gas is mixed with the motive water with or without a downstream static mixer in order to expose as many gas bubbles to the motive water for contact and dissolution. Some gases such as ozone are less soluble in water and only operate effectively at low gas:liquid ratios. Mechanical mixers and turbines are also used to disperse gas into the liquid of a mixing tank.

5.5.2 Contact tanks

Contact tanks are on the surface probably the simplest of all process tanks, but the internal hydrodynamics are often very complex and often neglected, and only discovered after construction. It is for this reason that contact tanks have been the subject of several case studies and a lot of research in the past.

Section 3.5.2 deals with the use of advanced modelling tools to ensure sufficient contact is available. Another tool that can be used, but only after the contact tank has been constructed, to establish contact time is a tracer test. A non-reactive salt is mixed into the inlet of the contact tank and the concentration is measured at the outlet of the tank over time. When the concentration is plotted against time a residence time distribution (RTD) curve is generated. Analysing the RTD curve can reveal many aspects relating to the hydrodynamic behaviour of the contact tank if the time is normalised by the theoretical retention time. If the first tracer is measured at a normalised time, $T = 1$, perfect plug flow is experienced. Should the first tracer be experienced almost immediately after injecting a tracer at, for example, $T = 0.1$ there is evidence of a short-circuiting in the contact tank. The time it takes for 10% of the tracer to reach the outlet has been defined as T_{10} . The T_{10} value has become an important performance indicator in calculating effective contacting time. An example of two RTD curves is shown in Figure 11.

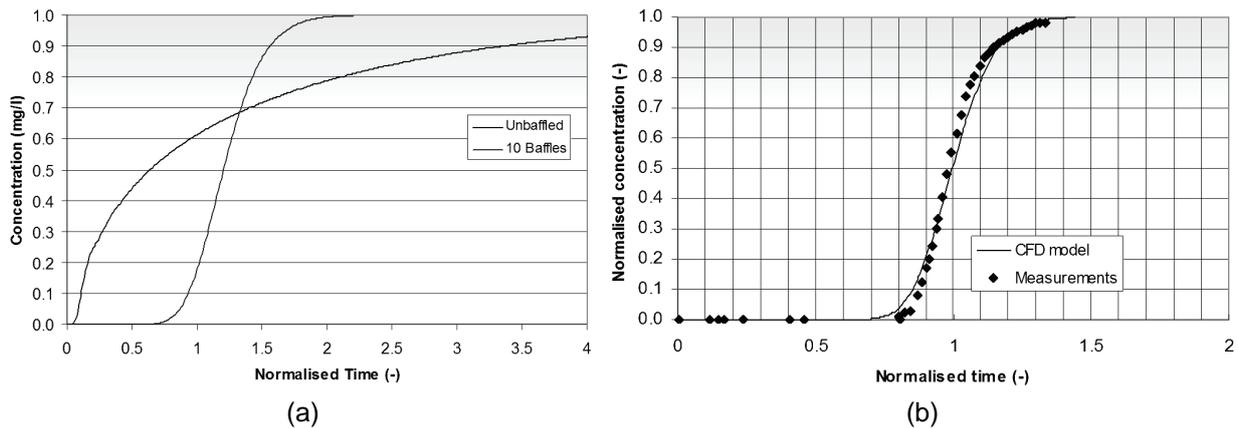


Figure 11 – Residence time distribution curve for a baffled and unbaflled clear water contact tank (a) and comparison of CFD model with experimental results (b) (van der Walt, 2002)

When calculating the effective contact time the theoretical contact time cannot be used, but T_{10} should be used. It has been shown that T_{10} is in some cases too conservative. The only way to ensure that contact tanks are hydraulically efficient is to make use of vertical or horizontal type serpentine baffles. Van der Walt (2008) has evaluated many different types of contact tanks to demonstrate the importance of hydraulic efficiency and the economic benefits that can be derived by including appropriately positioned and spaced baffles.

5.6 OXIDANT AND DISINFECTANT DOSING MAINTENANCE

Disinfection is one of the important, if not the most important, unit processes on a WTW. It is therefore one of the processes that needs to be operational at ALL times. In many cases it was found that the operators diligently ensured that all the unit processes are maintained properly only to allow the disinfection process to fail at the end of the treatment train. Disinfection systems should not only be designed with sufficient standby capacity but should also be maintained in order to ensure that the duty equipment as well as the standby equipment is available for use.

In order to ensure that disinfection systems are available at all times, the following basic actions should be implemented. (These activities apply equally to the full range of disinfection systems from small chlorine dosing units to large and complex ozonation systems).

- Keep copies of the operation and maintenance manual.
- Capture all equipment on an asset register with sufficient detail of all components.
- Establish a preventative maintenance plan based on the maintenance requirement of the supplier.
- Train the operators as well as the maintenance staff on how to operate and maintain the equipment.
- Budget, in time, to perform all the preventative and breakdown maintenance of the entire system.
- Ensure that sufficient critical spares and consumables are procured, in time, and stored in a place where the spares can be found. Replenish spares when necessary. It should also be noted that some spares have a shelf life and cannot be kept indefinitely.
- Monitor the execution of the maintenance plan and feedback from operating personnel.
- Monitor the availability of the equipment on a regular basis.
- Perform an annual performance audit on the disinfection equipment and emergency procedures and decide on suitability of equipment. Should replacement or upgrading be required project planning and budgeting should be initiated in time.
- Revise and improve the maintenance plan, budget and monitoring schedule annually.

Each oxidation and disinfection system presents unique maintenance challenges.

Even though ozone systems are complex, using highly technical instruments, the process is highly automated and very reliable, requiring only a modest degree of operator skill and time to operate a system. Maintenance on generators requires skilled technicians; if trained maintenance staff are not available at the plant, this work can be carried out by the equipment manufacturer. Therefore, backup units are usually installed to allow for instrument downtime. Generators should be checked daily when in operation. After a shutdown, dry air or oxygen should be allowed to flow through the generator to ensure that any moisture has been purged prior to energising the electrodes. At initial start up and after long down times, this process may take up to 12 hours, and usually longer when air is the feed gas. As an alternative, a small flow of dry air can be passed through the generator continuously when it is in standby mode to maintain the dry condition (USEPA, 1999).

Filters and desiccant in air preparation systems should be changed periodically, with the frequency depending on the quality of the inlet air and the number of hours in operation. Compressors require periodic service, depending on the type and operating time. Liquid oxygen tanks should be periodically pressure tested. Piping and contact chambers should be inspected periodically to check for leaks and corrosion.

CHAPTER 6 – CONSUMER HEALTH RELATED ASPECTS

- 6.1 - Introduction
- 6.2 - Health legislation
- 6.3 - Selected health related aspects

6.1 INTRODUCTION

In 1974, researchers in the Netherlands and the United States demonstrated that THMs are formed as a result of drinking water chlorination (USEPA, 1999). Trihalomethanes are formed when chlorine or bromide reacts with organic compounds in the water. The EPA subsequently conducted surveys confirming widespread occurrence of THMs in chlorinated water supplies in the US. The toxicology of THMs and other DBPs has since been the subject of extensive research. As a result of the DBP formed by chlorine, the most widely used disinfectant, the international water treatment industry placed much more emphasis on the use of alternative disinfectants. Unfortunately some of these alternative disinfectants have also been found to produce DBPs. These DBPs are either as a result of the reactions between disinfectants and compounds in the water or as a natural decay product of the disinfectant itself. The known DBPs are listed in Table 3. As stated in Chapter 3, the type and amount of DBPs produced during treatment depends largely on disinfectant type, water quality, treatment sequences, contact time, and environmental factors such as temperature and pH.

It is therefore of utmost importance when considering the use of chlorine and alternative disinfectants to ensure that the process responsible for the inactivation of pathogenic organisms is not compromised. Pathogens pose an immediate and critical public health threat due to the risk of an acute disease outbreak. Although most public health risks associated with DBPs are potentially chronic long-term risks, many systems will be able to lower DBP levels or revert to the use of alternative disinfectants without compromising microbial protection.

In order to emphasise the above statement, the findings from a recent WRC study by Freese and Nozaic (2005) is quoted.

Chloroform, which is the most commonly formed THM during chlorination, is a known carcinogen and can cause cancer ... This obviously caused concern amongst the water treatment fraternity and resulted in water treatment authorities reviewing chlorination practices in order to minimise THM formation and in 1978 the USEPA set maximum concentration limits for chloroform in potable water at 0.10 mg/L.

*However, chloroform is not considered an acute hazard to man at the low concentrations in which it is found in water ... In addition, despite rigorous scientific research studies, **no conclusive evidence has ever been found to prove that THMs, in the quantities in which they occur in drinking water, are harmful to humans.** ... For example, based on studies conducted on laboratory animals (mice, rats and rabbits) ... the margin of exposure for humans from the highest chloroform dose that produced no adverse effects, is estimated to be between 34 500 and 43 000 mg/kg per day. An average adult man, weighing between 70 and 90 kg, would have to drink ... around 1.5 L containing between 1 500 and 2 000 mg/L chloroform in order to ingest a dose the size of this margin of exposure. To further put the trihalomethane issue into perspective, consider the fact that a number of over-the-counter cough mixtures, available without prescription, contain chloroform in high concentrations. In order to ingest the same amount of chloroform as contained in a single dose (one or two teaspoons in most cases) of one of these cough mixtures, one would need*

to drink eight glasses of water per day for a year, assuming that the THM concentration of the water was at the maximum allowable limit of 100 µg/L.

The consequence of not striking a balance between the potential THM health effects and disinfection evokes some sobering thoughts (Freese and Nozaic, 2005).

It is incomprehensible that many people are so concerned about the health effects of THMs in their drinking water that they would consider not chlorinating their water, despite the fact that the many studies conducted to date have still failed to demonstrate any conclusive link between THMs in potable water and detrimental health effects, while overwhelming evidence exists to indicate the effectiveness of chlorine in destroying pathogenic organisms in water supplies. Still more surprising is that many of these people will happily smoke cigarettes at rates that numerous studies have clearly shown to drastically increase one's chances of contracting lung cancer. Unfortunately the media hype around the THM issue has been of such proportions that it has on occasion resulted in the obvious benefits of disinfection being disregarded in favour of their perceived dangers. Perhaps the most disastrous example of this occurred in Peru in 1991. Based on epidemiological evidence suggesting a statistically weak link between the consumption of chlorinated drinking water and liver cancer, Peruvian officials took the decision not to chlorinate much of their country's potable water supply. The ensuing cholera epidemic, which was a direct result of this decision, claimed some 4 000 lives.

The current status of health information on disinfectants and DBPs is summarised in Table 22. It is interesting to note that none of the disinfectants or DBPs fall in the human carcinogen classification, Group A. This group contains substances for which there is sufficient experimental evidence to establish a causal link between cancer and exposure. Most of the DBPs fall in Group B2, probable carcinogens, which means sufficient evidence exists based on exposure of animals to these substances. Unfortunately the exposure levels are not mentioned and the other health effects such as the mutagenicity, genotoxicity and teratogenicity are not mentioned.

Table 22 – Status on health information for disinfectants and DBPs
(Adapted from USEPA, 1999)

Contaminant	Cancer Classification ⁽¹⁾
Chloroform	B2
Bromodichloramethane	B2
Dibromochloramethane	C
Bromoform	B2
Monochloroacetic Acid	-
Dichloroacetic Acid	B2
Trichloroacetic Acid	C
Dichloroacetonitrile	C
Bromochloroacetonitrile	-
Dibromoacetonitrile	C
Trichloroacetonitrile	-
1,1-Dichloropropanone	-
1,1,1-Trichloropropanone	-
2-Chlorophenol	D
2,4-Dichlorophenol	D
2,4,6-Trichlorophenol	B2
Chloropicrin	-
Chloral hydrate	C
Cyanogen chloride	-
Formaldehyde	B2 ⁽²⁾
Chlorate	-
Chlorite	D
Bromate	B2
Ammonia	D
Hypochlorous acid	-
Hypochlorite	-
Monochloramine	-
Chloride dioxide	D

Notes

(1)	The scheme for categorising chemicals according to their carcinogenic potential is as follows:
	Group A: Human Carcinogen
	Sufficient evidence in epidemiologic studies to support causes association between exposure and cancer.
	Group B: Probable Human Carcinogen
	Limited evidence in epidemiologic studies (Group B1) and/or sufficient evidence from animal studies (Group B2)
	Group C: Possible Human Carcinogen
	Limited evidence from animal studies and inadequate or no data in humans
	Group D: Not Classifiable
	Inadequate or no human and animal evidence of carcinogenicity
	Group E: No Evidence of Carcinogenicity for Humans
	No evidence of carcinogenicity in at least two adequate animal tests in different species epidemiologic and animal studies.
	*EPA is in the process of revising the Cancer Guidelines Source USEPA, 1996
(2)	Based on inhalation exposure

6.2 HEALTH LEGISLATION

Apart from the mention that municipal health services are responsible to monitor the water quality and the general environmental pollution, the National Health Act of 2003 is silent on specific water health related issues. The Water Services Act (1997) and SANS 241 are, however more prescriptive and impose requirements on both chlorine residual as well as the limitation on THMs.

United States legislation is more specific and regulates the MCLs of a number of substances as indicated in Table 23. It should also be noted that the table indicates the potential health effects as well as the source of the DBP.

Table 23 – Disinfection by-products and potential health effects (Adapted from USEPA, 1999)

Compound	MCLG (mg/L)	MCL (mg/L)	Potential Health Effects	Sources of Drinking Water Contamination
Bromate	Zero ³	0.010 ²	Cancer	Ozonation by-product
Bromodichloromethane	Zero ³	see TTHMs	Cancer, liver, kidney, and reproductive effects	Drinking water chlorination and chloramination by-product
Bromoform	Zero ³	see TTHMs	Cancer, nervous system, liver and kidney effects	Drinking water ozonation, chloramination, and chlorination by-product
Chlorite	0.8 ³	1.0 ⁴	Haemolytic anaemia	Chlorine dioxide DBP
Chloroform	Zero ³	see TTHMs	Cancer, liver, kidney, reproductive effects	Drinking water chlorination and chloramination by-product
Dibromochloromethane	0.06 ³	see TTHMs	Nervous system, liver, kidney, reproductive effects	Drinking water chlorination and chloramination by-product
Dichloroacetic Acid	Zero ³	see HAA5	Cancer and other effects	Drinking water chlorination and chloramination by-product
Haloacetic Acids ¹ (HAA5)	N/A	0.060 ²	Cancer and other effects	Drinking water chlorination and chloramination by-product
Trichloroacetic Acid	0.3 ³	see HAA5	Possibly cancer and reproductive effects	Drinking water chlorination and chloramination by-product
Total Trihalomethanes ²	N/A	0.08 ⁴	Cancer and other effects	Drinking water chlorination and chloramination by-product

¹HAA5 is the sum of the concentrations of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.

²Total trihalomethanes are the sum of the concentrations of bromodichloromethane, dibromochloromethane, bromoform, and chloroform.

³Finalised on December 16, 1998 (63 RF 69390)

⁴Finalised on December 16, 1998 (63 FR 69390)

6.3 SELECTED HEALTH RELATED ASPECTS

6.3.1 Risk assessment

Different pathogens in the raw water include bacteria, protozoa, helminths and viruses. The typical concentrations of these pathogens in raw water vary significantly, from only a handful in the case of *Giardia* cysts and *Cryptosporidium* oocysts, to several billion organisms per 100 mL. The indicative infectious exposure also varies. Only a single *Giardia* or *Cryptosporidium* organism is required whereas millions of *Escherichia coli* are required for infection. It is also interesting to note that the pathogens that require the lowest infectious dose have been responsible for the largest number of incidents and cases in the USA (Conway *et al.*, 2008). It is therefore not surprising that the SDWA has promulgated legislation specifically targeting the treatment requirements for effective removal/inactivation of *Giardia* and *Cryptosporidium*. It is unfortunate that similar epidemiological data are not available in South Africa.

In cases where wastewater is planned for direct reuse it is recommended to perform both chemical and microbial risk assessments. Several risk assessment approaches have been developed, but it is important to apply an approach that has been developed for the water industry and covers all aspects, from the source to the end consumer's tap. Of particular importance when dealing with direct re-use, is the perception of potential consumers in accepting the principle of drinking treated wastewater. A number of case studies have been reported on direct re-use in the USA (Conway *et al.*, 2008). In these cases comprehensive risk assessments were performed not only in order to determine compliance with regulated substances, but also include a range of toxicological tests.

Future regulation in South Africa may also necessitate similar risk assessments as water resources are becoming more stressed and are increasingly being re-used, albeit indirectly.

It is hoped that more case studies can be developed in future to address some of these issues applicable to the South African context.

6.3.2 Health concerns related to specific disinfectants

The implementation or change of disinfectants requires special precautionary measures, as consumers may often complain not about the fact that the water is of poor quality, but simply because the water quality is different. Health concerns relating to possible DBP formation were discussed in Chapters 3 and 4. It is hoped that this section can also be expanded in future to make readers aware of the health impacts if disinfectants are not applied correctly, i.e. the balance between disinfection and DBP control is not managed effectively.

CHAPTER 7 – OCCUPATIONAL HEALTH AND SAFETY ASPECTS

- 7.1 - Introduction
- 7.2 - South African OHS legislation
- 7.3 - Other relevant legislation
- 7.4 - Substance specific safety concerns
- 7.5 - Material safety data sheets

7.1 INTRODUCTION

Not only is it essential to ensure that the health of the consumer is protected by understanding the health risks associated with insufficient disinfection, but also to protect the operating personnel handling the oxidants. The handling and storage of disinfectants and oxidants can be potentially fatal if not performed with the necessary care, as oxidants and disinfectants are by nature a threat to any form of life. The Occupational Health and Safety Act (1993) provides a framework for a safe working environment ensured by the identification of risks and putting into place appropriate mechanisms to remove, reduce or manage these risks. Chapter 7 will briefly outline the OHS Act and the relevant regulations, discuss other useful sources of information and attach material safety data sheets on the most commonly used oxidants and disinfectants.

7.2 SOUTH AFRICAN OHS LEGISLATION

7.2.1 Occupational Health and Safety Act

The Occupational Health and Safety Act (Act 85 of 1993) details amongst many aspects, the general duties of employers to their employees, and the general duties of employees at work, health and safety representatives and health and safety committees. The Act also makes provision for the development of regulations of which the following are relevant to this subject.

7.2.2 Regulations for Hazardous Biological Agents

This regulation is relevant to the organism that is being targeted. It provides a classification of hazardous biological agents (HBA), information and training, duties of persons who might be exposed to HBA, risk assessment by the employer, monitoring exposure at workplace, medical surveillance, personal protective equipment and facilities, labelling, packaging, transporting and storage, special measures for laboratories and industrial processes.

7.2.3 Construction Regulations

This regulation is relevant where the construction of a new plant is considered. It identifies the relationship between the client and the contractor. The requirements relating to various construction activities are explained.

7.2.4 Hazardous Chemical Substance Regulations

This regulation is of particular importance as it regulates many of the oxidants discussed in the previous chapters. Duties of persons who may be exposed to hazardous chemical substances (HCSs), assessment of potential exposure, air monitoring, chemical surveillance, respirator zones,

records, control of exposure to HCSs, personal protective equipment and facilities, maintenance of control measures, prohibitions, and disposal of hazardous chemicals are detailed.

Annexure 1 of the Regulation provides very specific guidelines regarding control of exposure to hazardous chemical substances. The occupational exposure limits (OELs) of several substances are listed in Table 24.

Table 24 – Occupational exposure limits of selected oxidants (OHSA, 1993)

Substance	Formula	TWA OEL-RL		Short term OEL-RL	
		Ppm	mg/m ³	Ppm	mg/m ³
Ammonia	NH ₃	25	17	35	24
Chlorine	Cl ₂	0.5	1.5	1	3
Chlorine dioxide	ClO ₂	0.1	0.3	0.3	0.9
Hydrogen peroxide	H ₂ O ₂	1	1.5	2	3
Ozone	O ₃	0.1	0.2	0.3	0.6

Annexure 1 also lists the requirements of MSDSs. Refer to section 7.5 for a list of applicable MSDSs.

7.2.5 General Machinery Regulations

This regulation provides information on notifiable substances. Table 25 lists the applicable notifiable substances.

Table 25 – Notifiable substances (OHSA, 1993)

United Nations Organisation Identification Number	Substance	Quantity and tonnage
1005	Ammonia (anhydrous, liquefied and solutions containing over 50% Ammonia)	20
1017	Chlorine	10

7.2.6 Major Hazardous Installations

An installation that presents a major hazard to the surrounding community may be classified as a major hazardous installation (MHI). A number of additional safety requirements are applicable to MHI installations. These regulations are often only applicable to installations where large quantities of a disinfectant such as chlorine are stored.

7.3 OTHER RELEVANT LEGISLATION

Depending on the industry and the particular application the following legislation may also be applicable:

- Mine Health and Safety Act, 1996 (Act No. 29 of 1996)
- Environment Conservation Act, 1989 (Act No. 73 of 1989)
- National Environmental Management Act, 1998 (Act No. 107 of 1998)
- Water Services Act, 1997 (Act No. 108 of 1997)
- National Water Act, 1998 (Act No.36 of 1998), in particular the Regulation on the registration of Water Care Works

The AWWA has also developed excellent resources relating to occupation health and safety. Some of the material will have to be adopted for South African conditions.

- *Safety Practices for Water Utilities* (AWWA, 2002) addresses safety issues for each of the main safety areas encountered in water utilities: hazardous materials, vehicles, hazardous energy, confined spaces, tools, facilities, personal protective equipment, construction sites, and respiratory equipment.
- *Emergency Planning for Water Utilities* (AwwaRF, 2001) presents techniques, forms, and principles for developing complete contingency plans for a variety of emergencies, from natural disasters to accidents caused by people. The manual can guide the identification of the most vulnerable portions of a system, depending on the type of disaster, and how to determine in what ways a disaster would likely affect services.

7.4 SUBSTANCE SPECIFIC SAFETY CONCERNS

The general approach to the handling of hazardous chemicals is to isolate the oxidant from the remainder of the plant. This implies a separate room or building that can isolate a potential spill or accidental release of gas. It is also recommended that the appropriate safety devices be installed on equipment and leak detection systems be put in place in generating and storage areas to warn operating personnel. The appropriate personal protective equipment, emergency kits and equipment to clean up a spill need to be provided. The requirements will differ depending on the installation and it is recommended to consult the supplier of the hazardous chemical/equipment as well as the relevant MSDS for specific details.

7.4.1 Chlorine based products

All direct exposure with the fumes of chlorine based products can be fatal and should be prevented. Proper storage and handling is therefore essential.

- **Chlorine gas** should be stored in a dedicated storage area that can be isolated in the case of a chlorine gas leak. Chlorine gas facilities should be equipped with gas leak detectors and alarms to warn operators of gas leaks.
- Bunded areas are required for the storage of **sodium hypochlorite**. In addition the on-site production of sodium hypochlorite needs to be approached with great care as hydrogen fumes present an explosion hazard.
- The on-site generation of **chlorine dioxide** also requires special care as it too is explosive at certain concentrations. Chlorine dioxide is considered explosive at concentrations which exceed 10% by volume in air, and its ignition temperature is about 130°C. Strong aqueous solutions of chlorine dioxide will release gaseous chlorine dioxide into a closed atmosphere above the solution at levels that may exceed critical concentrations.
- Storage of **calcium hypochlorite**, albeit in powder form, is also a major safety concern. Calcium hypochlorite should never be stored where it is subjected to heat or allowed to contact any organic material of an easily oxidised nature. Calcium hypochlorite should also be kept in sealed containers and away from equipment and exposed metal surfaces as the chlorine fumes can attack metal surfaces.
- A **chloramination** facility should include some safety provisions to prevent the formation of nitrogen trichloride and the vaporisation of ammonia at ambient temperatures. The possible formation of nitrogen trichloride at a chloramination facility should be considered when selecting sites for the ammonia and chlorine storage facilities. For this reason chlorine gas and ammonia gas should never be stored in the same room. The ammonia gas application points should be located at least 3 m away from chlorine feed solution lines. Anhydrous ammonia is lighter than

air, so any leaking vapour will rise quickly. Under pressure, anhydrous ammonia is a liquid. If the storage tanks and/or chemical feed equipment are installed indoors, ventilation and vapour detection devices should be located at high points in the room. The ventilation rates will vary, but typically, a minimum of six room changes per minute is recommended. Ammonia gas storage tanks should be protected from direct sunlight or direct sources of heat to avoid pressure increases in the tank. If not, ammonia gas may be released into the atmosphere through the pressure relief valves. In warm regions, outdoor tanks should be covered with a shelter or outfitted with a temperature control sprinkler system. Where fugitive emissions of ammonia are a concern, fume control may be required. If the accidental release from a storage container is a concern, an emergency scrubber system similar to a chlorine gas scrubber system should be considered. Special consideration should also be given to safety considerations at the off-loading point. Ammonia suppliers will be able to advise on the safety requirements.

7.4.2 Ozone

Ozone generators should be installed indoors for protection from the environment and to protect personnel from leaking ozone in the case of a malfunction. Ventilation should be provided to prevent excess temperature rise in the generator room, and to exhaust the room in the case of a leak. Adequate space should be provided to remove the tubes from the generator shell and to service the generator power supplies. Off-gas destruct units can be located outside if the climate is not too extreme. All rooms should be properly ventilated, heated, and cooled to match the equipment-operating environment, and equipped with an ambient ozone detector. Self-contained breathing apparatuses should be located in hallways outside the rooms liable to ozone hazards. The maximum short term exposure limit for ozone is 0.3 ppm (0.6 mg/m³) and the time weight average exposure limit is 0.1 ppm (0.2 mg/m³).

7.4.3 Hydrogen peroxide

Hydrogen peroxide is a strong oxidant and like all other oxidants should not be stored near heat sources or combustible material or oxidisable material as contact with such can lead to spontaneous ignition.

7.4.4 Potassium permanganate

On-site storage of potassium permanganate warrants careful consideration. Oxidants such as permanganate should be stored separate from organic chemicals such as polymers and activated carbon. Potassium permanganate can cause serious eye injury, is a skin and inhalation irritant, and can be fatal if swallowed. As such, special handling procedures include the use of safety goggles and a face shield, a specially approved dust mask, impervious gloves, coveralls, and boots to minimise skin contact.

7.4.5 Ultraviolet radiation

Ultraviolet lamps are mostly installed in a closed conduit, but some installations are installed in banks inside a channel. Direct exposure to the UV radiation source should be avoided. It is recommended that the original equipment manufacturer's operating and maintenance manual be consulted for more safety related detail.

7.5 MATERIAL SAFETY DATA SHEETS

The Hazardous Chemical Substances Regulation of the OHS Act requires the development of a MSDS for all hazardous chemicals. A MSDS contains essential information on the safe handling procedures, toxicological effects and emergency measures relating to hazardous chemicals. Examples of the most common substances can be easily downloaded from the Internet.

- Ammonium hydroxide - <http://www.sasol.com>
- Chlorine gas - <http://www.ncp.co.za/ProductsLCL.asp>
- Chlorine dioxide - <http://www.ncp.co.za/ProductsLCD.asp>
- Calcium hypochlorite - <http://www.hthscientific.co.za/ReadContent.aspx?id=137>
- Hydrogen peroxide - www.h2o2.com
- Hydrochloric acid - <http://www.ncp.co.za/ProductsHCL.asp>
- Ozone - <http://www.ncp.co.za/ProductsOZ.asp>
- Sodium hypochlorite - <http://www.ncp.co.za/ProductsSHC.asp>

CHAPTER 8 – SOUTHERN AFRICAN CASE STUDIES

- 8.1 - Introduction
- 8.2 - Case study 1 – Stilfontein WTW
- 8.3 - Case study 2 – Roodeplaat WTW
- 8.4 - Case study 3 – Vaalkop WTW
- 8.5 - Case study 4 – Rietvlei WTW
- 8.6 - Case study 5 – Goreangab WTW
- 8.7 - Case study 6 – Xstrata Elandplats WTW

8.1 INTRODUCTION

This section provides detailed information in a standardised format on a number of different case studies. It is intended to provide readers with an indication that the challenges faced by operators differ significantly and these challenges are dealt with in different ways.

The case studies currently include potable water treatment and industrial water treatment case studies. The following case studies were included:

No.	Name of case study	Responsible organisation	Water treatment type
1	Stilfontein WTW	Midvaal Water	Potable
2	Roodeplaat WTW	CoT	Potable
3	Vaalkop WTW	Magalies Water	Potable
4	Rietvlei WTW	CoT	Potable
5	Goreangab WTW	Windhoek Municipality	Potable
6	Eland Platinum WTW	Xstrata	Industrial

8.2 CASE STUDY 1 – STILFONTEIN WTW

Plant Name:	<i>Stilfontein WTW</i>	Submitted by:	<i>Marina Krüger</i>
Plant Capacity:	<i>250 ML/d</i>	Designation:	<i>Operations Manager</i>
Construction / commissioning date:	<i>Main plant: 1954 Intermediate ozone: 1985 Pre-ozone: 2008</i>	E-mail:	<i>marina@midvaalwater.co.za</i>
		Tel:	<i>018 482 1250</i>
Oxidant/s used:	<i>Ozone</i>	Date:	<i>September 2008</i>
Disinfectant/s used:	<i>Chlorine</i>		

8.2.1 Plant location

Midvaal Water Company was established in 1954 as an Article 21 Company and operates on a non-profit making basis. The plant is located on the northern bank of the Vaal River, about 15 km south east from Stilfontein in the North-West Province of South Africa. It draws raw water from the Middle Vaal section of the Vaal River, the section below the Vaal Barrage. During the course of time, the original treatment process has undergone various upgrades and expansions. These were necessary to keep up with the growing demand for potable water in the supply area as well as to cope with the ever-increasing pollution load of the raw water.

8.2.2 Plant purpose

Midvaal Water Company is charged with the responsibility for treatment and supply of bulk potable water to the Matlosana Municipality and various mining houses in the Klerksdorp-Orkney-Stilfontein-Hartbeesfontein area in the North West province of South Africa.

8.2.3 Source water characteristics and key challenges

At the time of plant construction in 1954, the raw water in the Vaal River was turbid and with a low organic content. Due to extensive industrialisation, urbanisation and agricultural developments in the catchments of the Vaal River since this time, the quality of the river water has changed significantly. Today, the river water at the abstraction point of Midvaal can be described as highly mineralised, hypertrophic and with high organic carbon and microbiological levels. The key source water parameters for the past five years are summarised in Table 26 as follows:

Table 26 – Key source water parameters at Stilfontein WTW

Parameter	Units	50 th Percentile	95 th Percentile
DOC	mg/L C	5.80	11.00
Turbidity	NTU	9.20	68.20
Chlorophyll-a	µg/L	51.00	130.00
Electrical conductivity	mS/m	77.00	96.00
Total alkalinity	mg/L CaCO ₃	148.00	170.00
Total hardness	mg/L CaCO ₃	241.00	338.00
Iron as Fe	mg/L	0.01	0.87
Manganese as Mn	mg/L	0.08	0.25
Colour	Hazen	65.00	150.00
pH	pH units	8.60	9.21
Ammonium as N	mg/L	0.30	0.70
Nitrate as N	mg/L	0.25	1.20
Ortho-phosphate as P	mg/L	0.32	0.53

8.2.4 Target contaminants/problem compounds

Some target pollutants requiring oxidation or both oxidation and disinfection are summarised in Table 27.

Table 27 – Target contaminants/problem compounds at Stilfontein and their required treatment: oxidation (indicated with letter O) or both oxidation and disinfection (indicated with letter B)

	Target level in treated product	Oxidation (O), disinfection (D) or both (B)
Chlorophyll-a (µg/L)	<0.5	O
DOC (mg/L)	<10	O
Fe (mg/L)	<0.2	O
Mn (mg/L)	<0.1	O
Colour (Hazen)	<5	B
Tastes and odours	No MIB and Geosmin detected	O
<i>Giardia</i> and <i>Cryptosporidium</i>	0 cells/10 L	B
Faecal coliform bacteria	0 cells/100 mL	B

8.2.5 Treatment processes employed

The processes used at Stilfontein WTW are summarised in Table 28.

Table 28 – Treatment processes employed at Stilfontein WTW

Process	Treatment objective
Pre-ozonation	Reduction of chlorophyll, colour removal
Coagulation	Flocculation of suspended particles
DAF	Removal of floatable, light organic flocs and algae
Intermediate ozonation	Oxidation of complexes of manganese and iron, colour, tastes and odours, viruses and protozoan parasites
Secondary chemicals addition	Flocculation of oxidised Mn, Fe and particulate matter
Sedimentation	Removal of flocculated particles
Rapid sand filtration	Final barrier for micro-organisms and removal of remaining fine particles
Chlorination	Removal of harmful micro-organisms, disinfection

8.2.6 Description of oxidation and disinfection equipment/technologies used

The key technology aspects of oxidation and disinfection equipment/technologies are summarised in Tables 29 and 30 respectively.

Table 29 – Equipment/technologies used in the oxidation process at Stilfontein WTW

Oxidation process: ozone	
Capacity:	3 x 8 kg/h generators
Equipment type:	Dielectric ozone generators
Dose range:	Pre-ozone: 0.5 to 1.5 mg/L Intermediate ozone: 2.0 to 2.5 mg/L
Feed source (e.g. air, oxygen, LOX):	Oxygen from a PSA plant
Contactator type:	Pre-ozone reactor: radial diffuser Intermediate ozone reactor: deep U-tube
Residence time:	Pre-ozone: 2 minutes Intermediate ozone: 4 minutes
Transfer efficiency:	Pre-ozone: ±92% Intermediate ozone: 98%
By-product/off-gas handling:	Thermal catalytic destructor (pre-ozone reactor) and dilution (U-tube reactor)
Dosing control:	Proportional to flow
Material of construction:	Concrete reactors, 316 stainless steel pipe work, oxygen and/or ozone approved ancillaries

Table 30 – Equipment/technologies used in the disinfection process at Stilfontein WTW

Disinfection process: chlorine	
Capacity:	3 dosing points each of 30 kg/h
Equipment Type:	Gas chlorinators and ejectors
Dose range:	0.5 to 6 mg/L
Feed source (e.g. air, oxygen, LOX):	Chlorine gas in 907 kg drums
Residence time:	1 hour
Dosing control:	Proportional to flow as well as the residual chlorine concentration

8.2.7 Type of monitoring performed

Water is sampled three ways:

Compliance sampling on the treated water: Potable water has to comply with the latest SANS 241 standard. Monitoring is conducted in conformance to this standard which prescribes levels of compliance for the different physical, chemical and biological parameters as well as the frequency of sampling. Results are submitted monthly to the National Drinking Water Quality Monitoring program of DWAF. Weekly samples are also taken in the distribution process for quality assurance purposes.

Compliance sampling of raw water and plant residue streams: Target Water Quality Objectives were set for the particular catchment. The river water is therefore monitored extensively and data are used to determine trends and emerging quality issues that might need additional/further treatment. As the filter backwash water and treated sludge supernatant are recycled to the inlet of the treatment plant, the quality of all waste streams is monitored.

Process optimisation sampling: Water samples are collected at set intervals at all the different treatment processes for optimisation purposes and quality control and assurance. The quality of the raw water source is also monitored three-hourly for timely detection of changes in water quality.

8.2.8 Key challenges of oxidation and disinfection processes and technology

The source water is of a very complex nature due to extensive upstream pollution. It is not uncommon to have high levels of DOC, high concentrations of algae and their related products, etc. coinciding with colour, manganese and iron. The levels of these substances do not only vary seasonally, but also as a result of periodic point – and diffuse pollution. The different processes are not equally successful in removing the full suite of target substances and it is more beneficial to optimise a specific process for specific substances. For example, pre-ozone for chlorophyll removal; DAF for removal of algal cells and turbidity; intermediate ozone for removal of organic complexes of manganese and iron, colour, taste and odour, etc. The water recycled from the filter backwash and sludge treatment processes also contains high levels of dissolved iron and manganese, algae, micro-organisms, etc. This combined recycle stream is therefore treated with chlorine and is then introduced prior to the pre-ozone reactor to ensure additional treatment thereof. The frequency and duration of taste and odour problems are increasing and the current plant setup is not able to eliminate these compounds completely. The use of PAC/GAC is considered for future. Another challenge is the re-growth of bacteria in the distribution network in summer as a result of the high ambient temperature and high organic content of the final product. A project is planned for 2009 to investigate the characteristics and extent of biofilms growth in the distribution network.

8.2.9 Capital and operating cost

At the time of construction of the intermediate reactor and generation facility in 1985, the capital outlay for the oxidation process was R 5 million. This was to treat 120 ML/day at a maximum ozone concentration of 4 mg/L. A second U-tube reactor was added in 1993 to handle approximately another 120 ML/d at a cost of ±R2 million. The ozone plant was upgraded from 2006 to 2008 with new generators, a PSA plant and a pre-ozone reactor at a cost of R14.7 million. The operating costs in Table 31 include maintenance costs and cost of electricity for the oxidation process for 2008.

Table 31 – Operating costs of Stilfontein WTW

Process	Dosing rate	Energy consumption		Energy cost as proportion of total operating cost	Maintenance cost as proportion of total operating cost
	(mg/L)	kWh/kL	kWh/kg	%	%
Ozonation	2.8	0.07	34.4	72	28

8.2.10 Recent improvements and lessons learned on ozone production

The type of compressors, oil (synthetic vs. mineral oil) and filter systems installed will determine the quality of the feed air being produced as well as the maintenance requirements and associated costs. As this feed air quality determines the efficiency of oxygen generation as well as the lifespan of the adsorbent in the PSA tanks, care should be taken to ensure that the right equipment is selected for air preparation. In this case, water and oil vapour contaminated the adsorbent in the PSA tanks due to inadequate and incorrect filters.

It is very important to ensure that all critical operating parameters/conditions are continuously monitored and recorded in order to detect potential problems in time. At Stilfontein, a comprehensive checklist was developed in conjunction with the suppliers of all the equipment for the operators as well as the maintenance teams.

Reliable and adequate operational and quality control data assist in the optimal operation and cost efficient use of the ozone facility.

8.2.11 Future plans

Pilot studies on the efficiency and benefits of split-dosing of ozone indicated that 30 to 40% more chlorophyll could be removed through a dose rate of 1.0 to 1.5 mg/L applied as pre-ozone. Higher dosages did not remove significantly more chlorophyll, but an increase in DOC values was evident at higher pre-ozone dosages. The full-scale pre-ozone process has only been in operation since July 2008. As the raw water quality varies seasonally, the full impact of the pre-ozone process on all the target contaminants will only be known over time. The extent of pollution and emerging water quality problems will also dictate future extensions and process adjustments.

8.3 CASE STUDY 2 – ROODEPLAAT WTW

Plant Name:	<i>Roodeplaas WTW</i>	Submitted by:	<i>Ms. Leanne Coetzee</i>
Plant Capacity:	<i>60 ML/d</i>	Designation:	<i>Deputy Director: Scientific Services</i>
Construction / commissioning date:	<i>September 2005</i>	E-mail:	<i>leannec@tshwane.gov.za</i>
Oxidant/s used:	<i>KMnO₄, Chlorine</i>	Date:	<i>March 2009</i>
Disinfectant/s used:	<i>Chlorine, UV</i>		

8.3.1 Plant location

The Roodeplaas WTW treatment plant is located in close proximity to the Roodeplaas Dam in the Pienaars River catchment, approximately 25 km north of Pretoria. The first phase of the Roodeplaas WTW was completed in September 2005.

8.3.2 Plant purpose

The Roodeplaas WTW was constructed to augment the water supply to the northern parts of the Pretoria distribution system and also to reduce the dependence on Rand Water as the major water source. At the time, the northern suburbs received water from Rand Water, Rietvlei WTW and a number of boreholes.

8.3.3 Source water characteristics and key challenges

The key source water parameters are summarised in Table 32 and are typical of many eutrophic water sources in the country.

Table 32 – Key source water parameters at Roodeplaas WTW

Parameter	Units	50 th Percentile	95 th Percentile
TOC	mg/L C	6.86	8.96
Turbidity	NTU	3.50	33.25
Chlorophyll-a	µg/L	5.30	34.00
TDS	mS/m	317.60	356.40
Total alkalinity	mg/L CaCO ₃	148.90	173.20
Total hardness	mg/L CaCO ₃	128.50	151.40
Iron as Fe	mg/L	0.16	0.88
Manganese as Mn	mg/L	0.19	0.40
Colour	Hazen	33.40	144.00
pH	pH units	8.08	8.93
Ammonium as N	mg/L	0.62	1.27
Nitrate as N	mg/L	0.25	1.20
Ortho-phosphate as P	mg/L	0.19	0.32

8.3.4 Treatment processes employed

The current and planned unit treatment processes employed at Roodeplaat are summarised below:

Table 33 – Treatment processes employed at Roodeplaat WTW

Process	Treatment objective
Pre-treatment	Screening of debris
Pre-oxidation (KMnO ₄)	Oxidation of iron and manganese, taste and odour control
Pre-ozonation*	Taste and odour control, iron and manganese oxidation, DOC fractionation, colour reduction, chlorophyll-a reduction
Aeration	Removal of volatile organic substance, iron oxidation
Coagulation	pH correction and coagulation of suspended solids
Flocculation	Flocculation of suspended solids
DAF	Removal of algae and floatable suspended solids
Upflow clarification	Removal of flocculated particles (capturing of PAC dosed at inlet if KMnO ₄ is not dosed), taste and odour control and DOC removal
Rapid Sand filtration	Barrier for micro-organisms and removal of remaining fine particles
Ozonation*	Taste and odour removal and inactivation of <i>Cryptosporidium</i> and <i>Giardia</i>
GAC filtration*	Removal of DOC and taste and odour compounds
UV irradiation	Inactivation of harmful micro-organisms such as <i>Cryptosporidium</i> and <i>Giardia</i>
Chlorination	Inactivation of harmful micro-organisms and establishment of disinfectant residual
Chloramination*	Establish disinfectant with longer 'shelf life'

* Planned for future implementation

8.3.5 Description of oxidation and disinfection equipment/technologies used

The key technology aspects can be summarised in Table 34 as follows.

Table 34 – Equipment/technologies used in the oxidation and disinfection processes at Roodeplaat WTW

	Oxidation: KMnO ₄	Oxidation: pre-ozone (future planning)	Disinfection: UV radiation	Disinfection: chlorine	Disinfection: chloramination	Disinfection: ozone (future planning)
Type	Alldos diaphragm pumps	Sidestream injector/static mixer	ATG Willand	V10K	Alldos dosing pumps	
Dose range	0-2 mg/L	0-3 mg/L	0-40 MJ/cm ²	0-15 kg/hr	0-2 mg/L	0-6 mg/L for disinfection
Feed source (e.g. air, oxygen, LOX)	KMnO ₄ powder and make-up tank	LOX	1 UV bank	2 banks of 3 off 1 ton liquid chlorine cylinders	Ammonium hydroxide	LOX
Dosing control	Manual setpoint and SCADA flow paced	Manual setpoint SCADA flow paced	Automatic radiation output adjustment for varying transmissivity	Flow paced with SCADA dosing rate setpoint	Automatic residual setpoint and flow paced control	Residual chlorine feedback control
Capacity			1 off 60 ML/d per bank	3 x 15 kg/hr Wallace and Tiernan	2 x 30 l/h	2 x 20 kg/hr
Mixer / contactor type			NA	Venturi injector and submerged sparge pipe in chlorine contact tank	In suction pipeline of high lift pumps	Bubble diffuser
Contact time			***	2 hours chlorine contact time in baffled chlorine contact tank	N/A	12 minutes

8.3.6 Key challenges of oxidation and disinfection processes and technology

The source water occasionally contains high levels of iron, manganese, taste and odour and algae concentrations. Potassium permanganate is used successfully to oxidise the occasional high iron and manganese levels. An additional aeration step was added to oxidise easily oxidisable volatile organics followed by the injection of pulverised activated carbon (PAC) for occasional taste and odours. In order to maximise the use of PAC a solids contact clarifier was included to recover and recycle PAC from the clarifier. Disinfection is achieved with UV radiation as primary disinfection followed by chlorine disinfection with a contact time of 2 hours and chloramination before leaving the WTW.

8.3.7 Capital and operating cost

The 60 ML/d plant was constructed in 2005 for R 150 million. The operating cost varies depending on the chemicals and processes in use. The plant is currently operated by Magalies Water as an agent for the City of Tshwane. The operating costs were not available at the time.

8.3.8 Planned improvements

City of Tshwane initiated, in line with all other City of Tshwane operated plants, a process to implement ozonation and GAC in order to meet future water quality challenges. The engineering is at an advanced stage and the upgrade is planned to be completed within the next two years.

8.4 CASE STUDY 3 – VAALKOP WTW

Plant Name:	<i>Vaalkop WTW</i>	Submitted by:	<i>M Dayanand</i>
Plant Capacity:	<i>210 ML/d</i>	Designation:	<i>Area Manager</i>
Construction / commissioning date:	<i>Plant 1: 1970, Refurbished 2007 Plant 2: 1981, 1986, 1991 Plant 3: 1999</i>	E-mail:	<i>mukeshd@magalieswater.co.za</i>
Oxidant/s used:	<i>Chlorine and ozone</i>	Date:	<i>March 2009</i>
Disinfectant/s used:	<i>Chlorine</i>		

8.4.1 Plant location

The Vaalkop WTW treatment plant is located directly next to the Vaalkop Dam in the Hex- and Elands river catchments. The first phase of the Vaalkop WTW was built in 1970 and subsequently expanded and upgraded in six phases. The latest phase included a process upgrade of the first phase. The plant is located approximately 120 km from Thabazimbi and about 50 km from Rustenburg. The residence time of the treated water in the pipelines is therefore relatively long.

8.4.2 Plant purpose

The Vaalkop WTW was initially constructed to supply water to the Union Platinum mine near the town of Northam. Subsequent upgrades supplied water to more mines and towns in the Rustenburg, Northam and Thabazimbi area. All the water supplied is potable water.

8.4.3 Source water characteristics and key challenges

At the time of construction of the Vaalkop Dam the source water was of a pristine nature with an electrical conductivity of approximately 40 mS/m, originating from the Rustenburg and Koster areas. The yields of the Hex and Elands rivers became insufficient and were later augmented by a canal system linking the Vaalkop Dam with Hartbeespoort Dam via the Roodekopjes Dam. The source water gradually changed from pristine to highly eutrophic. Table 40 shows the key source water parameters for the past three years.

Table 35 – Key source water parameters at Vaalkop WTW

Parameter	Units	50 th Percentile	95 th Percentile
DOC	mg/L C	8.14	8.55
Turbidity	NTU	5.66	16.62
Chlorophyll-a	µg/L	32.45	43.70
Electrical conductivity	mS/m	71.15	87.61
Total alkalinity	mg/L CaCO ₃	36.72	128.94
Total hardness	mg/L CaCO ₃	27.87	216.56
Iron as Fe	mg/L	0.05	0.16
Manganese as Mn	mg/L	0.02	0.11
Colour	Hazen	30.00	60.00
pH	pH units	8.14	8.55
Ammonium as N	mg/L	0.17	0.44
Nitrate as N	mg/L	0.10	0.49
Ortho-phosphate as P	mg/L	0.20	0.80

8.4.4 Target contaminants/problem compounds

Some target pollutants requiring oxidation or both oxidation and disinfection are summarised in Table 36.

Table 36 – Target contaminants/problem compounds at Vaalkop Dam and their required treatment: oxidation (indicated with letter O) or both oxidation and disinfection (indicated with letter B)

Table 36 – Target contaminants/problem compounds at Vaalkop and their required treatment

	Target level in treated product	Oxidation (O), disinfection (D) or both (B)
Chlorophyll-a (µg/L)	<1	O
DOC (mg/L)	<10	O
Fe (mg/L)	<0.2	O
Mn (mg/L)	<0.1	O
Colour (Hazen)	<10	O
Tastes and odours	<10 ng/L MIB and Geosmin detected	B
Giardia and Cryptosporidium	0 cells/10 L	B
Faecal coliform bacteria	0 colonies/100 mL	B

8.4.5 Treatment processes employed

The processes employed at Vaalkop WTW are summarised below:

Table 37 – Treatment processes employed at Vaalkop WTW

Plant	Process	Treatment objective
2,3	Pre-chlorination	
1	Pre-ozonation	Oxidation of iron and manganese and organic compounds, colour removal, aid flocculation
2,3	PAC adsorption	Taste and odour removal, algal toxin adsorption
1,2,3	Coagulation	Destabilisation of suspended matter
1,2	DAF	Removal of floating flocs and algae
2,3	Sedimentation	Removal of heavier flocculated particles
3	Cocodaff	Simultaneous floatation and filtration – removal of floatable flocs and algae at the top and gravity filtration of micro particles and micro organisms
1	Intermediate ozonation	Oxidation of taste and odour compounds, inactivation of viruses and parasites
1	GAC filtration	Adsorption of oxidised organic compounds
1,2	Rapid sand filtration	Removal of micro particles and micro organisms
1,2,3	Chlorination	Disinfection of bacteria and micro organisms
2,3	Chloramination	Providing residual disinfectant in long distribution system

8.4.6 Description of oxidation and disinfection equipment/technologies used

The key technology aspects of treatment at Vaalkop can be summarised as follows:

Table 38 – Equipment/technologies used in the oxidation and disinfection processes at Vaalkop WTW

	Oxidation: ozone	Oxidation: chlorine	Disinfection: chlorine	Disinfection: chloramination
Equipment type	Wedeco ozone generators	Gas chlorinators and vacuum injectors	Gas chlorinators and vacuum injectors	Diaphragm dosing pumps
Dose range	Pre-ozonation: 0.5-1.0 mg/L Inter ozonation: 1-2 mg/L	1-4 mg/L	1-7 mg/L	4:1 chlorine to ammonia ratio as Cl. Average dose approximately 2 mg/L.
Feed source (e.g. air, oxygen, LOX)	Compressor generated air	Chlorine gas from 925 kg drums	Chlorine gas from 925 kg drums	25% ammonia solution from bulk tanks
Product				Ammonium hydroxide 25% solution
Capacity	2 x 9 kg/h generators	30 kg/h	60 kg/h	1200 mL/min
Mixer / contactor type	Pre-ozonation: static mixer Intermediate ozonation: contact tank	Direct injection into raw water pipeline	Baffled clear water tank	Dosed after post chlorination before high lift pumps. Contact immediate at inlet pipe to pumps.
Transfer efficiency	Pre-ozonation: ±90% Inter ozonation: 98%			
Contact time		15 min	1.5 hours	Immediate reaction
By-product handling:	Thermal catalytic destructors			
Dosing control	Fixed rate proportional to flow	Proportional to flow and residual chlorine concentration	Proportional to flow and residual chlorine concentration	Proportional to free chlorine reading from online analyser. Average of 4:1 chlorine to ammonia.
Material of construction	Concrete reactors; 316 stainless steel pipework			

8.4.7 Key challenges of oxidation and disinfection processes and technology

The source water occasionally contains high levels of iron and manganese. Plants 2 and 3 utilise pre-chlorination for this purpose; however, in cases where taste and odour problems occur at the same time as iron and manganese, either pre-chlorination or PAC can be used. The water recycled from the sludge dams also contain high levels of dissolved iron as well as taste and odours. The other key challenge is that high taste and odour compounds often coincided with a high chlorine demand. Dosing PAC therefore delayed the introduction of a pre-chlorination step in which oxidation of organic and inorganic material can occur. Plant 1 was recently retrofitted with processes that can address this challenge. For this purpose a pre-ozonation step was introduced (to address the pre-oxidation requirements). The main disinfection step was introduced downstream of the DAF. The adsorption step was also changed to GAC filters at the end of the process train. Secondary disinfection was achieved with chlorine. A chloramination step ensured that a disinfectant residual is maintained in the long distribution system.

Another challenge faced by the Vaalkop distribution system is the long residence times. It is common knowledge that nitrification can occur in distribution systems when using chloramines. Nitrification is accelerated in cases where free ammonia occurs, high water temperatures and high chlorine demand. Difficulties were experienced maintaining adequate chlorine residual values in summer especially when PAC was used.

8.4.8 Capital and operating cost

When constructed in 2006, the capital outlay for the ozonation process was approximately R 10.5 million. Operating cost varies depending on the chemicals and processes used at the time. Table 39 below lists the approximate unit operating cost of the different oxidation and disinfection processes.

Table 39 – Operating costs of Vaalkop WTW

Process	Dosing Rate (mg/L)	Chemical cost (R/kg)	Maintenance cost (R/kg)	Energy cost (R/kL)	Unit Cost (R/kL)
Chlorination	8	10.00	0.05	0.01	0.08
Ozonation	2.5	Not available at the time			
Ammonia	2	1.50	0.01	0.005	0.01

8.4.9 Recent improvements and lessons learned

The recent plant upgrade demonstrated a number of water quality improvements. Table 40 lists the difference between the raw and potable water quality of the three plants.

Table 40 – Raw water quality and potable water quality from the three plants at Vaalkop WTW

Parameter	Raw Water	Plant 1	Plant 2 & 3
DOC (mg/L)	8	5	7
Iron (mg/L)	0.10	0.01	0.04

Water quality problems in the treatment plant or in the distribution system require a review of the entire water system. Problems cannot be addressed symptomatically. Particular care should be given to internal waste streams that are being re-used. These are often the cause of the most severe treatment challenges especially in temperate climates and eutrophic waters. A long-term view is required when making process decisions in cases where water is abstracted from a source receiving effluent from developing areas. It is unlikely that the water quality will improve and short-term

solutions will only result in fruitless expenditure. The introduction of any new process or upgrade needs to be properly investigated both for the selection of appropriate equipment as well as water quality.

8.4.10 Future plans

The processes employed at Plant 1 will be assessed over time. The demographics of the customer base and water quality objectives will dictate future process upgrades. Possible extension of ozone dosing from Plant 1 to the raw water inlet at Plant 2 is considered.

8.5 CASE STUDY 4 – RIETVLEI WTW

Plant Name:	<i>Rietvlei WTW</i>	Submitted by:	<i>Carel Taljaard Leanne Coetzee</i>
Plant Capacity:	<i>40 ML/d</i>	Designation:	<i>Deputy Director: Own Water Sources Deputy Director: Scientific Services</i>
Construction / commissioning date:	<i>20 ML/d (1934) 10 ML/d Fountain water DAF (1990) GAC (1999) Ozone (2009)</i>	E-mail:	<i>carelt@tshwane.gov.za leannec@tshwane.gov.za</i>
		Tel:	<i>012 358 1803 012 358 1802</i>
Oxidant/s used:	<i>Chlorine, ozone</i>	Date:	<i>March 2009</i>
Disinfectant/s used:	<i>Chlorine Monochloramine Ozone (future)</i>		

8.5.1 Plant location

The Rietvlei water treatment plant is located next to the eastern side of Rietvlei dam. The plant is located some 25 km from the centre of Pretoria, at coordinates: S 25°52'40.32, E 28°15'52.56.

8.5.2 Plant purpose

Pretoria obtains its water from six sources – Rand Water, fountain water, boreholes and treated water from three own sources (Rietvlei WTP, Roodeplaat WTP and the Temba WTP). Treated water from the Rietvlei dam is pumped to various reservoirs where it mixes with water from Rand Water. The blending ratio is about 70% Rand Water and 30% from own sources. The water supplied by Rietvlei is of potable quality.

8.5.3 Source water characteristics and key challenges

The first process configuration of the Rietvlei WTP consisted of sedimentation and sand filtration (1932). The catchment area of the Rietvlei dam is relatively small and stretches only to Kempton Park, and during winter times the majority of the inflow to the dam consists of treated sewage. In the 1980s the dam turned eutrophic and it was decided to retrofit the process train by installing dissolved air flotation to cater for the increasing load of algae from the dam. This was one of the first applications of a full scale DAF plant in South Africa and the process was furthermore installed in the same volume as the filter basins (known as DAFF – dissolved air flotation / filtration). The prolonged drought in the mid 1990s saw an increased load of treated sewage water entering the dam and the situation

worsened when the natural wetland upstream of the dam, which removed nutrients such as phosphates and nitrates, failed. The N:P ratio in the dam changed and it was also seen that the sediments in the dam actually started releasing bound phosphates. This led to an increased concentration of blue green algae in the water, and the associated taste and odour problem, together with concerns regarding organic contaminants emanating from the recycled sewage water, led to the installation of a GAC process step. This additional process step was commissioned in 1999. More concern over the presence of pathogens and the fact that ozone became more cost effective, led to a decision in 2006 to install ozone as an additional barrier. The addition of this process unit is currently being implemented.

The key source water parameters are summarised in Table 41 (values taken for the 2008 calendar year):

Table 41 – Key source water parameters at Rietvlei WTW

Parameter	Units	Year average	Maximum
TOC	mg/L C	9.09	12.44
Turbidity	NTU	4.59	12.69
Chlorophyll-a	µg/L	64.95	369.14
Electrical conductivity	mS/m	40.65	46.20
Total alkalinity	mg/L CaCO ₃	133.24	162.52
Total hardness	mg/L CaCO ₃	119.58	242.11
Iron as Fe	mg/L	0.34	7.00
Manganese as Mn	mg/L	0.16	0.38
Colour	Pt/cobalt units Hazen	33.61	69.34
pH		7.70	9.08

8.5.4 Treatment processes employed

The processes used at Rietvlei WTW are summarised in Table 42.

Table 42 – Treatment processes employed at Rietvlei WTW

Process	Plant 1990	Plant 1999	Plant 2010	Treatment objective
Pre-chlorination				
Pre-ozonation				Killing of algae, oxidation of Fe and Mn
PAC adsorption				
Coagulation				Agglomeration of micro particles into flocs
Sedimentation				
DAFF				Removal of small suspended floatable particles
Ozonation				Inactivation of pathogens, oxidation of organics including taste and odour
Sand filtration				Removal of small suspended particles
GAC filtration				Adsorption of organic material
Chlorination				Primary disinfection
Chloramination				Secondary disinfection

8.5.5 Description of oxidation and disinfection equipment/technologies used

The key technology aspects of treatment at Rietvlei are summarised in Table 43.

Table 43 – Equipment technologies used in the oxidation or disinfection process at Rietvlei WTW

	Oxidation: ozone	Oxidation: chlorine
Capacity	3 × 10 kg/h (two duty one standby)	Post-chlorine – 20 kg/h
Type	Still to be decided	Gas
Dose range	Up to 18 mg/L – The ozone demand was tested to be 0.52 mg O ₃ /mg DOC	Post chlorine – 3 mg/L
Feed source	Possibly LOX	
Mixer / Contactor type	Pre-ozone – static mixer Main ozone – radial mixers and baffled contact tank	Post chlorine – in tank
Residence time	Pre-ozone – less than 30 seconds Main ozone – 20 minutes	Post chlorine – 2 ML contact time (65 min)
Dosing control	Pre-ozone – fixed dosage, linked to flow variation Main ozone – feedback control base done by residual ozone concentration in water (also redox potential change)	Post-chlorine – fixed dosage, linked to flow variation
Storage	Possibly cryogenic tank	350 years

8.5.6 Key challenges of oxidation and disinfection processes and technology

Rietvlei dam is eutrophic, and has elevated levels of DOC (sometimes as high as 15 mg/L). Concern over high levels of organics, tastes and odours, and associated contaminants from treated sewage water such as endocrine disruptors and medicinal components led to the decision to install GAC, and at a later stage, ozone. A key challenge is to manage the GAC filters such that the beneficial biological culture is established and maintained on the media. This is done by regular backwashing with water, maintenance wash by air, and regeneration of the GAC. Each GAC filter is regenerated at a frequency of about 4 years. The installation of ozone will complement the GAC filters in that the organics will be oxidised to a more assimilative state (for the biological culture) and to smaller organic compounds which is more readily adsorbed onto the GAC. A key challenge will be to apply the correct dose in achieving this goal.

Due to the mixing of final Rietvlei water with Rand Water, it is necessary to chloramine the water to fit in with the disinfection practiced by Rand Water.

8.5.7 Capital and operating cost

The 1999 upgrade in installing GAC was at a cost of R 40 million. The addition of ozone in 2010 need an estimated outlay of around R 23 million. This cost includes other civil additions such as laboratory and office areas. The operating costs are listed in Table 44.

Table 44 – Operating costs of Rietvlei WTW

Process	Dosing Rate (mg/L)	Chemical cost (R/kg)	Maintenance cost (R/kL)	Energy cost (R/kL)	Unit Cost (/kL)
Chlorination	5	9.62	<0.005		0.05
Ozonation	1.5 – pre ca 5 – main	30.00	0.02	0.04-0.07	35

8.5.8 Recent improvements and lessons learned

The 1999 upgrade with GAC was preceded by a pilot plant study which indicated that some 20-25% removal in organics, measured as DOC and chlorine demand, could be expected. In practice, about 10-15% removal of these targeted compounds was achieved. The occurrence of taste and odour incidents, however, was completely eliminated. Problems were experienced on-site with GAC media losses (about 20% per annum) and a rigid monitoring programme was installed to try and quantify the areas where these losses are experienced. It was seen that the physical regeneration process accounted for about half of these losses and the other half was due to backwash losses. The levels of the GAC in the filters were allowed to drop from 1.5 m to about 1.2 m which provided in total a freeboard in the filters of about 1m. This proved to be manageable in curbing excessive losses of carbon.

8.5.9 Future plans

The main upgrade at Rietvlei during the following two years will be the installation of an ozonation process. A monitoring process will be planned to measure performance for the first year of running and to determine the impact of the ozone on the performance of the GAC.

Although ammoniation has been installed at Rietvlei, the process still needs to be commissioned and used. In order to align the disinfection regime with that used by Rand Water, this system will be put into operation soon.

8.6 CASE STUDY 5 – GOREANGAB WTW

Plant Name:	<i>Goreangab WTW</i>	Submitted by:	<i>Erich Konige</i>
Plant Capacity:	<i>21 ML/d</i>	Designation:	<i>Plant Manager</i>
Construction / commissioning date:	<i>21 ML/d (2001)</i>	E-mail:	<i>truddy@wingoc.com.na</i>
		Tel:	<i>+264 (0) 61 272138 / 272083</i>
Oxidant/s used:	<i>Chlorine, ozone, hydrogen peroxide, sodium hypochlorite</i>	Date:	<i>March 2009</i>
Disinfectant/s used:	<i>Chlorine Ozone</i>		

8.6.1 Plant location

The new Goreangab water treatment plant is located towards the north-western side of Windhoek, some 10 km from the centre of the city, at coordinates: S 22°31'35.01, E 017° 0'17.85.

8.6.2 Plant purpose

The capital of Namibia obtains the bulk of its potable water requirements from the Von Bach Regional Water Scheme, some 70 km due north of Windhoek, which mainly consists of the Von Bach, Swakoppoort and Omatako Dams. Two of the city's own sources are the borehole scheme (south of Windhoek), and the Goreangab Water Reclamation Plant, west of Windhoek, which only contribute approximately 20% of the total bulk water requirements during normal years, i.e. with sufficient water supply.

Due to an increasing demand on water sources, Windhoek makes use of a direct reclamation configuration where sewage water is first treated in a conventional activated sludge treatment process. The purified sewage water and eutrophic water from the adjacent Goreangab Dam can be blended or treated separately by the New Goreangab Water Reclamation plant. The old Goreangab Water Reclamation plant is currently used to treat the same water up to a standard which can be used for irrigation of parks, while the final water from the new treatment plant is blended with water from the Von Bach scheme in a ratio not exceeding 35% reclaimed water.

8.6.3 Source water characteristics and key challenges

The source water for the new Goreangab WTP is obtained from the Gammams sewage treatment plant. After the activated sludge process, the water is discharged to a series of maturation ponds from where the water flows via a closed pipeline to the reclamation plant. At the plant, the purified sewage water is blended with water from the Goreangab dam in the raw water sump.

The challenge with direct reclamation has always been to obtain the buy-in of the community to the idea. Since the commissioning of the first reclamation plant in Windhoek in the late 1960s, the citizens of Windhoek have embraced this principle and have developed a certain sense of pride in practicing reclamation. At the same time, the Municipality of Windhoek has specified very strict water quality parameters after each treatment process to ensure the multiple barrier principle.

The key source water parameters are summarised below in Table 45 (the values are taken from the report from which the process design was derived. Values shown are for the 50th and 95th percentile).

Table 45 – Key source water parameters at Goreangab WTW

Parameter	Units	Median	95 th percentile	Median	95 th percentile
		Goreangab dam		Gammams sewage plant	
DOC	mg/L C	31.40	43.00	36.00	43.63
Turbidity	NTU	18.55	102.22	1.90	3.70
Chlorophyll-a	µg/L	9.92	46.86	8.51	24.11
TDS	mg/L	270.00	344.50	624.00	781.00
Alkalinity	mg/L CaCO ₃	122.60	153.10	202.70	282.30
Iron as Fe	mg/L	0.83	5.30	0.11	0.38
Manganese as Mn	mg/L	0.31	1.62	0.03	0.17
Colour	Hazen	25.00	80.00	50.00	63.75
Ammonia as N	mg/L	0.57	1.74	0.16	2.86
<i>E. coli</i>	100mL	10	36650	236	4044
Faecal coliforms	CFU/100 mL	8	37400	395	7183

8.6.4 Treatment processes employed

The treatment processes employed at Goreangab are summarised in Table 46.

Table 46 – Treatment processes employed at Goreangab WTW

Process	WTP	Treatment objective
PAC adsorption		Removal of organic content
Pre-ozonation		Killing of algae, oxidation of Fe and Mn
Coagulation		Agglomeration of micro particles into flocs
Sedimentation		Not required
DAF		Removal of small suspended floatable particles
Sand filtration		Removal of small suspended particles
Ozonation		Inactivation of pathogens, oxidation of organics including taste and odour
BAC filtration		Biological removal of organic material
GAC filtration		Adsorption of organic material
Ultrafiltration		Disinfection, removal of fine suspended particles
Stabilisation		Stabilise water with NaOH
Chlorination		Disinfection

8.6.5 Description of oxidation and disinfection equipment/technologies used

Table 47 shows a summary of key technology aspects for equipment and technologies in use at Goreangab.

Table 47 – Equipment technologies used in the oxidation or disinfection process at Goreangab WTW

	Oxidation: ozone	Disinfection: chlorine
Capacity	3 x 6 kg/h (two duty one standby)	Post-chlorine – 3 kg/h
Type	Ozonia ozonators	Gas
Dose range	Up to 20 mg/L	Post chlorine – 5 mg/L
Feed source	Air – with on-site PSA units	Post chlorine – in baffled tank
Mixer / Contactor type	Pre-ozone – static mixer Main ozone – radial mixers and baffled contact tank	Post chlorine – 60 min
Residence time	Pre-ozone – about 1 minute Main ozone – 20 minutes	Post-chlorine – fixed dosage, linked to flow variation
Dosing control	Pre-ozone – variable dosage, linked to flow variation Main ozone – feedback control base done by residual ozone concentration in water	35 days
Storage	PSA units with no storage	

8.6.6 Key challenges of oxidation and disinfection processes and technology

The initial installation of pre-ozone was for a dosage of up to 2 mg/L. It was found over time that a higher dosage employed here has beneficial effects in the removal of organic material and overall conditioning of the water downstream of the process. The dosage has since been doubled to an average pre-ozone dosage of approximately 4 mg/L.

Enhanced coagulation is also practiced at the plant where some 80 mg/L ferric chloride (measured as Fe) is dosed to facilitate organic removal. This is beneficial later on in the process where the load on the ozone dosage and the activated carbon replenishment rate is alleviated.

Provision is made for three ozone dosing points at the main ozone contact tank. It has been found that an average dose of around 4 mg/L of ozone is needed at the first dosing point, while an average of about 1.5 mg/L is then required at the second dosing point. The third dosing point is seldom used as the ozone residuals are too high for the Biological Activated Carbon (BAC) process. A big challenge is to automate the operation of the main ozone dosing regimen and residual ozone meters, which provide feedback to the ozonators, may be used in the water. The maintenance of the meters is however troublesome and the possible use of redox meters to assist in the operation of the ozone plant currently being investigated.

The production of concentrated oxygen as feed to the ozonators remains troublesome and this has led to a bottleneck in water production since not enough feed gas could be supplied to the ozonators.

An important final barrier regarding the disinfection of biological pathogens is the UF process and although teething problems regarding capacity of the plant were experienced at start-up, these have been rectified and the current operation of this unit is regarded as crucial in maintaining the integrity of the plant.

8.6.7 Capital and operating cost

The 2001 cost of the new Goreangab water reclamation facility was R 120 million. The plant can produce 21 ML/d but is currently producing 15-16 ML at a total cost of between N\$ 4.00 and 5.50/kL.

8.6.8 Recent improvements and lessons learned

- DAF: desludge system and saturator system was improved – the DAF is a critical process in direct reclamation.
- The use of ozone and related bromate formation potential should be taken seriously during plant design.
- All concrete structures were rehabilitated with special corrosion resistant material – corrosion risk throughout the entire plant must not be underestimated during plant design.
- The BAC process serves a special purpose for long term granular activated carbon savings.

8.6.9 Future plans

Due to the increasing TDS in potable water production through reclamation, side-stream low pressure reverse osmosis will be considered in future. This will also reduce the bromate concentration and any other potentially harmful parameters.

8.7 CASE STUDY 6 – XSTRATA ELANDPLATS WTW

Plant Name:	<i>Eland Platinum WTW</i>	Submitted by:	<i>Dr Fanie Botha</i>
Plant Capacity:	<i>4 ML/d potable 11 ML/d industrial</i>	Designation:	
Construction / commissioning date:	<i>2008</i>	E-mail:	<i>fbotha@xstrata.co.za</i>
Oxidant/s used:	<i>Chlorine dioxide</i>	Date:	<i>March 2009</i>
Disinfectant/s used:	<i>Chlorine dioxide</i>		

8.7.1 Plant location

Eland Platinum mine is located near Brits in the North West province next to the N4 Platinum Highway.

8.7.2 Plant purpose

At the time when the mine was planned, the local municipality did not have water services available and the mine decided to abstract raw water from a nearby irrigation canal and purify this water to two different quality standards. The industrial standard was used for the processing of the ore and the potable water standard was used for human consumption, and special make-up water and cooling water.

8.7.3 Source water characteristics and key challenges

The irrigation canal from which water is abstracted originates from the Hartbeespoort Dam. This water is renowned for its algal blooms, high chlorophyll-a values, algal toxins and taste and odours. The water entering the canal is drawn from a lower level in the dam and differs in some respects from the water at the surface. A snapshot of the canal data was taken during 2007 and the key parameters are listed in Table 48.

Water is also taken from a number of boreholes around the mine. The boreholes were constructed as a dewatering measure, but also serve as an additional water source. The key characteristics of the borehole water are high salinity and nitrates.

The canal water and borehole water are mixed in a quarry before being piped to the water treatment plant.

Table 48 – Key source water parameters at Eland Platinum WTW

Parameter	Units	Grab sample canal
DOC	mg/L C	7.70
Turbidity	NTU	13.00
Chlorophyll-a	µg/L	9.00
Electrical conductivity	mS/m	55.00
Total alkalinity	mg/L CaCO ₃	136.00
Total hardness	mg/L CaCO ₃	241.00
Iron as Fe	mg/L	0.20
Manganese as Mn	mg/L	0.17
Colour	Hazen	28.00
pH	pH units	7.80
Ammonium as N	mg/L	0.40
Nitrate as N	mg/L	4.00
Faecal coliforms	CFU/100 mL	150

8.7.4 Target contaminants / problem compounds

Target contaminants / problem compounds that require oxidation are listed in Table 49 (indicated with letter 'O') and/or disinfection (indicated with letter 'D') or both (indicated with letter 'B')

Table 49 – Target contaminants/problem compounds at Eland Platinum WTW and their required treatment

	Target level in treated product	Oxidation (O), disinfection (D) or both (B)
Chlorophyll-a (µg/L)	<0.5	O
DOC (mg/L)	<10	O
Fe (mg/L)	<0.2	O
Mn (mg/L)	<0.1	O
Colour (Hazen)	<5	B
Tastes and odours	No MIB and Geosmin detected	O
<i>Giardia</i> and <i>Cryptosporidium</i>	0 cells/10 L	B
Faecal coliform bacteria	0 colonies/100 mL	B

8.7.5 Treatment processes employed

The processes used at the Eland Platinum WTW are summarised in Table 50.

Table 50 – Treatment processes employed at Eland Platinum WTW

Process	Treatment Objective
Pre-oxidation (chlorine dioxide)	Reduction of chlorophyll-a, colour removal, iron and manganese oxidation, disinfection of faecal coliform
Coagulation	Flocculation of suspended particles
DAF	Removal of floatable, light organic flocs and algae
Rapid Sand filtration	Final barrier for micro-organisms and removal of remaining fine particles
Granular Activated Carbon adsorption/filtration	Adsorption of taste and odour compounds, algal toxins and DOC removal (also acts as an additional filtration step)
Chlorination using hypochlorite tablets	Disinfection of harmful micro-organisms, disinfection

8.7.6 Description of oxidation and disinfection equipment/technologies used

The key technology aspects are shown in Table 51.

Table 51 – Equipment/technologies used in the oxidation and disinfection processes at Eland Platinum WTW

	Oxidation: chlorine dioxide	Disinfection: chlorine
Capacity	350 m ³ /h	
Type	Siemens	Hypochlorite dissolving units
Dose range	0 to 3 mg/L	0 to 6 mg/L
Feed source	Sodium chlorate and hydrochloric acid	Ca(OCl) ₂ tablets
Mixer / Contactor type	Inline diffuser	
Residence time	1 minute	1 hour
Residence time	Manual with online chlorine residual instruments	
Dosing control		Manual

8.7.7 Key challenges of oxidation and disinfection processes and technology

The water entering the plant can vary significantly. In cases where the borehole water is used the water is crystal clear with very little suspended solids. In cases where canal water is used the water changes drastically and requires extensive treatment to remove suspended organic and inorganic matter. Water mixed in the quarry is the worst, as this is a mixture of high salinity water and water with all the qualities of the canal water. The operator therefore needs to adjust the plant dosing rates every time the source changes.

8.7.8 Capital and operating cost

The plant was constructed for about R 70 million in 2007. The operating and maintenance was contracted out at the time and the unit costs were not available.

8.7.9 Lessons learned and future plans

A number of lessons were learned since the commissioning of the water treatment plant. Apart from the possibility to expand the plant should the platinum production increase, the mine has also considered a number of options to construct treatment streams for specific needs. One possibility is to introduce a dedicated high quality potable water stream that will only be used for human consumption. This potable water stream could include more advanced oxidation and disinfection technology such as ozone and automated chlorine dosing.

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