THE PREDICTION FOR CHLORINE DECAY FROM POTABLE WATER IN PIPELINE SYSTEMS

WRC Report

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by

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EXECUTIVE SUMMARY

1. General background and motivation of the project:

The quality control and modelling of water quality in distribution systems is a relatively new field. Realising that the water quality after treatment is not a guarantee for the water reaching the consumer's tap, it has become necessary to attend to this problem. It is increasingly important to design and manage distribution systems carefully to ensure safe drinking water up to the consumer's tap.

The decay of chlorine concentration is one of the well-known and most important changes to occur in distribution systems. Three groups in the water supply field have a direct interest in predicting chlorine concentration:

(a) Operators must ensure that enough chlorine is added to the water in the treatment plant to maintain a residual when the water reaches the consumer at a later stage. The water cannot be returned to the purification plant once it is on its way to the consumer. If the chlorine content is not sufficient the operator must act quickly to rectify the problem.

(b) Process designers do not have a reliable mathematical model for the prediction of chlorine losses in pipeline systems. In long distribution systems, it must already be decided during the design stage whether to chlorinate the water only at the origin or to make use of secondary chlorination along the way.

(c) Network designers make extensive use of hydraulic considerations, but up to now could not place the same emphasis on quality considerations. The integration of water quality models with hydraulic network models makes it possible to calculate the average age of the water at the withdrawal points in order to control the maximum age of the water in the distribution system, thus adding an additional constraint on network design.

The starting point to resolve these problems is the analysis of the decay rate of chlorine in water. Three factors influence chlorine decay:

(a) The reaction between the chlorine and the impurities in the water is the first factor affecting chlorine decay. This reaction is independent of the medium through which the water flows.

(b) The second important factor is the reaction between the chlorine and the pipe wall. It is a function of the area/volume relationship of the pipe, the pipe material and the presence and nature of biofilm on the pipe wall.

(c) The radial diffusion of the chlorine from the centre of the pipe towards the pipe wall could be a third contributing factor. The diffusion coefficient is dependent on the turbulence in the pipe, the pipe diameter and temperature, and is not thought to be a critical parameter for larger water supply pipelines.

2. Objectives of the study:

Before any of the above proposals can be implemented to predict chlorine losses in complex distribution systems, it is necessary to develop and verify a mathematical model for the simplest case; a single pipe. In terms of the original contract with the Water Research Commission, the objectives of this study were therefore to:

(a) Apply a comprehensive three-parameter chlorine decay rate model to the simplest case of a single pipeline.

(b) Develop procedures for the standardised measurement or calculation of the model parameters.

(c) Verify the mathematical model for a number of water types, pipeline types, temperature and chlorine species.

3. Summary of the major findings and conclusions reached:

The conclusions drawn from the results presented in this project are summarised below.

3.1. Conclusions on the measurement of chlorine decay:

(a) All the chemical reactions associated with free chlorine and monochloramine do not occur at the same rate. To eliminate the initial fast reactions from the medium and long term reactions, the first free chlorine reading was only taken after the first hour, and thereafter at hourly intervals. In the case of monochloramine, the first reading was taken after four hours, and thereafter at four-hourly intervals.

(b) A good estimate of free chlorine decay can be made if the experimental test is continued for a period of eight hours (or longer). For monochloramine, the test period should be at least 24 hours at four-hourly intervals, and at daily intervals thereafter for five days or longer.

(c) In this study, excellent results were obtained if three initial chlorine concentrations were used. For free chlorine, the initial concentrations used were fixed at 2, 4 and 8 mg/l above the 20-minute breakpoint. In the case of monochloramine, the initial concentrations were fixed at 2, 4 and 8 mg/l as Cl_2.

3.2. Conclusions on the modelling of chlorine decay:

(a) For both free chlorine and monochloramine, substantially better data fits were obtained if a n^{th}-order decay rate model were used instead of the customary first order decay rate model.

(b) The reaction orders are different for different water sources, and even different for the same water source at different times. For a given sample, however, the reaction orders are independent of temperature.

(c) The rate constants, in all cases, are dependent on temperature. The higher the temperature, the higher the decay rate constants.

(d) The reaction order for free chlorine varied from 0.36 to 1.22, with no apparent underlying pattern. For monochloramine, the reaction order fell into two distinctively different categories. For monochloramine decay up to 24 hours (medium-term tests), the reaction order varied from 0.02 to 0.25. For monochloramine decay from 24 hours onwards (long-term tests), the reaction order varied from 0.92 to 0.95.

3.3. <u>Conclusions on free chlorine decay in pipelines:</u>

(a) The free chlorine decay rates obtained in pipelines were higher than in parallel bulk decay rate tests, indicating that the pipe walls did contribute significantly to the total decay of free chlorine.

(b) On the assumption that the bulk decay reaction order is equal to one, the mass transfer coefficient between the bulk flow and pipe wall could be calculated. With the exception of a single outlier, the coefficient varied between 0.0065 m/h and 0.0457 m/h.

4. <u>Review of project in terms of the initial objectives:</u>

In terms of the original contract with the Water Research Commission, the objectives were to:

(a) Apply a comprehensive three-parameter chlorine decay rate model to the simplest case of a single pipeline. The three-parameter model is based on the assumption of first-order kinetics. As will be shown further on, this assumption was not found to be the best model for the experimental data gathered. The three-parameter model could not be adapted and had to be simplified to a two-parameter pipeline model. The two-parameter model was successfully applied to and calibrated for two full-scale pipelines.

(b) Develop procedures for the standardised measurement or calculation of the model parameters. This objective was fully met, with comprehensive test procedures for the decay of free chlorine as well as monochloramine.

(c) Verify the mathematical model for a number of water types, pipeline types, temperature and chlorine species. The mathematical model for chlorine decay was verified for four diverse raw water types, for two chlorine species, and at three different temperatures. The pipeline tests were conducted for two pipelines, on four different occasions, but only for free chlorine. The decay of monochloramine was too slight to allow precise measurements within the pipeline tests sections.

The following important contribution was made, over and above that anticipated at the start of the project:

(a) The reaction order of the decay of both free chlorine and monochloramine deviates substantially, which is commonly accepted by many workers in this field. The incorporation of nth-order reaction kinetics into some of the existing mathematical models is quite complicated, and could lead to substantially different results.

(b) It is important to eliminate the initial fast reactions from the data set from which the medium term chlorine decay is estimated. Failure to do so will significantly distort the reaction order as well as the rate constant.

(c) Monochloramine shows two clearly different sets of behaviour. Up to 24 hours, the reaction order is below 0.3 and there are significant differences between different water sources. After 24 hours, the decay rates for different sources are essentially the same, and the reaction order very close to one.

5. Recommendations for future study:

(a) The effect of secondary chlorination on different source waters should be studied as to give network operators a practical guide on the possible implementation thereof. In other words, if secondary or tertiary chlorination is practised, will the chlorine decay at the same rate?

(b) More direct methods of estimating pipe wall-related chlorine reaction constants are needed, e.g. conducting a practical test on the pipe wall itself.

(c) The use of strategically placed sensors in the distribution system coupled with remote telemetry might offer a way to perform continuous on-line calibration of network chlorine decay models as conditions change over time.

(d) The present water quality models for distribution systems, which all assume first order bulk decay, should be updated for n^{th}-order decay to give more realistic results.

THIS REPORT IS PRESENTED IN TWO PARTS:

PART 1

FULL REPORT: **THE PREDICTION OF CHLORINE DECAY FROM POTABLE WATER IN PIPELINE SYSTEMS**

PART 2

COMPANION DOCUMENT TO THIS REPORT:
PRACTICAL GUIDELINE

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4. Materials and methods

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7. Conclusions and recommendations

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LIST OF SYMBOLS

- ***First order, 3 parameter model:***

ε = fractional error

λ = root of Bessel equation

Δr^* = incremental distances at r^*

ΔX^* = incremental distances at X^*

A_0 = dimensionless parameter (= $L^*D/r_0^{*2}U^* = \pi L^*D/Q$)

A_1 = dimensionless parameter (=kL^*/U^*)

A_2 = dimensionless parameter (= $V_d^*r_0^*/D$)

C = dimensionless chlorine concentration (= C^*/C_0)

C_0 = inlet chlorine concentration (mg/l)

C_{av} = dimensionless cup-mixing average concentration (= C_{av}^*/C_0)

D = effective diffusivity of chlorine species in water (m^2/s)

$f(r^*)$ = flow parameter term depending on the flow regime

(a) laminar flow: $f(r^*) = 2[1-(r^*/r_0^*)^2]$

(b) turbulent flow: $f(r^*) = 1$

J_0 = Bessel function of the first kind of order zero

J_1 = Bessel function of the first kind of order one

k = first order decay rate constant in the bulk water (1/s)

L^* = pipe length (m)

Pe_a = axial Peclet number (= L^*U^*/D)

Q = flow rate throughout the system (m^3/s)

r = dimensionless radial distance from the centre of the pipe (= r^*/r_0^*)

r^* = radial distance from the centre of the pipe (m)

r_0^* = pipe radius (m)

U^* = average flow velocity throughout the distribution system (m/s)

V_d^* = chlorine consumption rate at the pipe wall (m/s)

X = dimensionless axial distance from the inlet along the pipe (= X^*/L^*)

X^* = axial distance from the inlet along the pipe (m)

The superscript * denotes a dimensional quantity.

- ***First order, 2 parameter model:***

ν = kinematic viscosity of water (m^2/s)
$\theta(c)$ = decay rate of the first order, 2 parameter model
A = cross-sectional flow area of the pipe (m^2)
c = chlorine concentration in bulk flow (mg/l)
c_w = chlorine concentration at the wall (mg/l)
D = molecular diffusivity of chlorine in water (m^2/s)
d = pipe diameter (m)
k_b = first-order bulk reaction rate constant (1/s)
k_f = mass transfer coefficient
k_f = mass transfer coefficient between bulk flow and pipe wall (m/s)
L = pipe length (m)
q = flow rate (m^3/s)
Re = Reynolds number [= $qd/(A\nu)$]
R_H = hydraulic radius of pipe (m) [= pipe radius/2]
Sc = Schmidt number [= ν/D]
Sh = Sherwood number

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CHAPTER 1

INTRODUCTION

1.1. Background:

The quality control and modelling of water quality in distribution systems is a relatively new field. Realising that the water quality after treatment is not a guarantee for the water reaching the consumer's tap, it has become necessary to attend to this problem. It is increasingly important to design and manage distribution systems carefully to ensure safe drinking water up to the consumer's tap.

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The starting point to resolve these problems is the analysis of the decay rate of chlorine in water. Three factors influence chlorine decay:

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(c) The radial diffusion of the chlorine from the centre of the pipe towards the pipe wall is the third contributing factor. The diffusion coefficient is dependent on the turbulence in the pipe, the pipe diameter and temperature.

1.2. Problem statement:

Before any of the above proposals can be implemented to predict chlorine losses in complex distribution systems, it is necessary to develop and verify a mathematical model for the simplest case; a single pipe. In terms of the original contract with the Water Research Commission, the objectives of this study are therefore to:

(a) Determine typical chlorine decay constants for free and combined chlorine on representative pipeline systems.

(b) Predict chlorine decay in existing and proposed pipelines by using a computerised program.

Some of the aspects not included in this paper are summarised below:

(a) It is not the intention of this project to predict the primary chlorine demand by using other water quality parameters. It merely deals with the aspect of predicting chlorine loss in pipeline systems in terms of loss coefficients used in a mathematical model.

(b) It does not deal with the formation and kinetics of disinfection by-products but rather with the amount of chlorine consumed.

(c) The study only deals with the measuring of chlorine compounds - not the measuring of microbiological parameters to determine the effect of residual chlorine concentrations.

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CHAPTER 2

LITERATURE REVIEW

2.1. Chemistry of chlorination:

2.1.1. Reactions with water:

Chlorine, added to water either as a gas or liquid, hydrolyzes to form hypochlorous acid (HOCl) and hydrochloric acid (HCl). One atom is oxidised to Cl^+, the other reduced to Cl^- (White, 1992). The reaction is as follows:

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \qquad (2.1)$$

$$K_h = \frac{[H^+][Cl^-][HOCl]}{[Cl_2]} = 4*10^{-4} \qquad (at\ 25^\circ C) \qquad (2.2)$$

The equilibrium of this reaction is in favour of free Cl_2 since $K_h << 1$. These often result in development of compounds such as nitrogen trichloride, NCl_3. To minimise these effects, a high quality water is often used as chlorinator feed water. Flash mixing is required at the point where the chlorine water is applied to prevent the development of localised low pH conditions in order to eliminate the possibility of chlorine losses. In dilute solution and at pH levels above about 4, the equilibrium shown in equation (2.1) is displaced greatly to the right and very little Cl_2 exists as such in solution (White, 1992).

The HCl that is formed, is completely dissociated under usual dilute aqueous solution conditions. However, hypochlorous acid is a relatively weak acid and is very poorly dissociated at pH levels below 6 (Sawyer, McCarty, 1978).

$$HOCl \leftrightarrow H^{+} + OCl^{-},\ pK_a = 7.5 \qquad (2.3)$$

Equations (2.1) and (2.3) therefore indicate that the relative amount of the various oxidised chlorine species is a function of the pH of the water (White, 1992).

From the pK_a value (at 25°C) the assumption can be made that at pH 7.5 the activities of HOCl and OCl^- are equal. When the pH drops below 7.5, HOCl predominates while OCl^- is the predominant species at pH above 7.5 (White, 1992). It is therefore evident that HOCl can react in three different directions:

(a) At high pH levels (pH > 8) OCl^- predominates the reaction.
(b) At low pH levels (pH < 8) the reaction is predominated by HOCl.
(c) At very low pH levels (pH < 1) the reaction is predominated by Cl_2.

The distribution of the various chlorine species with pH can be illustrated using a distribution diagram in which the fraction of the total aqueous chlorine (particularly the species Cl_2, HOCl, or OCl^-) is plotted against the pH of the water for a fixed Cl^- concentration.

Figure 2.1 shows that under typical natural water conditions, HOCl and OCl^- are the major chlorine species. Cl_2 is unimportant at pH above 2. In the pH range of 6 to 9 for natural waters, the relative amounts of HOCl and OCl^- are very sensitive to pH. HOCl and OCl^- differ greatly in their ability to disinfect water, so that pH control can be a critical factor in determining the degree of disinfection achieved by a certain level of chlorine (White, 1992). At a low pH, the disinfection ability of HOCl is strong while the disinfection ability of OCl^- is weak.

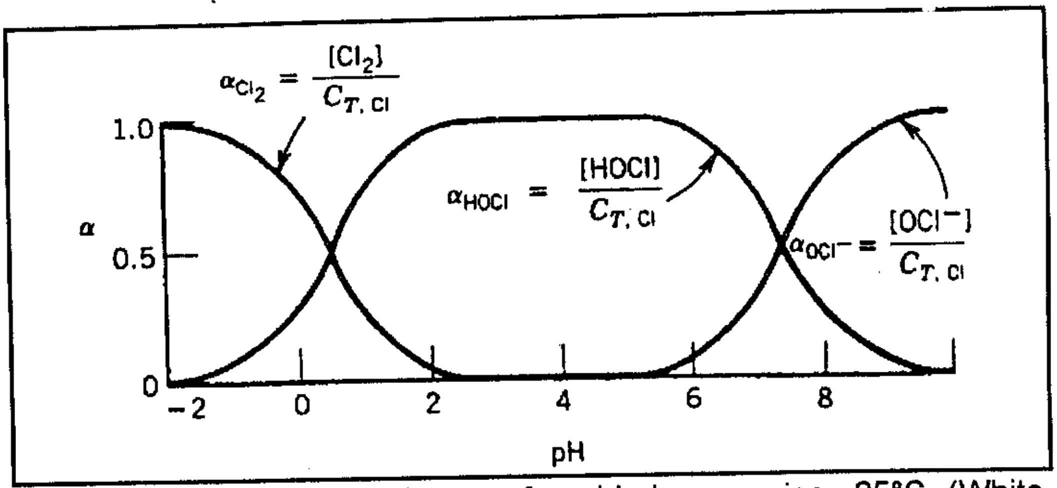

Figure 2.1. Distribution diagram for chlorine species, 25°C (White, 1992)

It is thus evident that the equilibrium of the above mentioned reactions is influenced by three parameters namely:

(a) The pH of the water
(b) The water temperature
(c) The Cl_2 - concentration.

The form in which chlorine is added to a water affects some of the chemical properties of the water. The addition of chlorine gas to a water will lower its alkalinity because of the production of the strong acid and HOCl by the reaction in equation (2.1) (White, 1992). However, if chlorine is dosed as sodium hypochlorite (household bleach) the following two reactions describe the process:

$$NaOCl \rightarrow Na^+ + OCl^-$$
$$OCl^- + H_2O \leftrightarrow HOCl + OH^-$$

By using calcium hypochlorite (HTH) the total hardness of a water is increased.

$$Ca(OCl)_2 \rightarrow Ca^{2-} + 2OCl^-$$
$$2OCl^- + 2H_2O \leftrightarrow 2HOCl + 2OH^-$$

These considerations are important because they show that the form in which chlorine is added can affect the water chemistry in different ways (White, 1992).

2.1.2. Reactions with ammonia:

The reactions of chlorine with ammonia and organic nitrogen are quite different from those of chlorine with other inorganic and organic compounds. The most important of the reactions of chlorine with nitrogen compounds is that of hypochlorous acid with ammonia (White, 1992).

Chlorine reacts with ammonia to produce a series of chlorinated ammonia compounds called chloramines and eventually oxidises the ammonia to nitrogen gas (N_2) or a variety of nitrogen-containing chlorine-free products (White, 1992). Table 2.1 shows the chloramines formed in the reaction between chlorine and ammonia.

Table 2.1. Products formed in the reaction between chlorine and ammonia

Name	Formula
Monochloramine	NH_2Cl
Dichloramine	$NHCl_2$
Trichloramine / Nitrogen trichloride	NCl_3

The products of the reaction vary with conditions such as the pH, ratio of Cl_2 added to ammonia present, and contact time. As higher chlorine to ammonia-nitrogen ratios are reached, the ammonia is eventually oxidised to nitrogen gas (N_2), a small amount of nitrate (NO_3^-), or a variety of nitrogen-containing inorganic oxidation products (Montgomery, 1985).

The formation of the chloramines can be depicted as a stepwise process as follows:

$$\begin{aligned} &NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O \\ &NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O \\ &NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O \end{aligned} \tag{2.4}$$

The rate of the first step, the formation of monochloramine, is very much dependent on the pH of the solution. The maximum rate occurs at a pH of 8.3 and decreases rapidly at higher and lower pH values. The rate of the reaction also varies greatly with the temperature (Fair *et al*, 1948).

The general statement that dichloramine is formed predominantly at low pH values (5.0 - 6.5) and monochloramine at high pH values (greater than 7.5) can be interpreted in terms of the equilibrium reaction:

$$2NH_2Cl + H^+ \Leftrightarrow NH_4^+ + NHCl_2$$

An excess of hydrogen ions should displace this reaction to the right, yielding greater amounts of dichloramine at lower pH values. This equation also predicts that the relative proportions of monochloramine and dichloramine should be affected not only by the pH, but also by the excess ammonia present. This has been confirmed by the spectrophotometric measurements (Fair *et al*, 1948), which also give a value of $6.7*10^5$ for the equilibrium constant, K, where:

$$K = \frac{[NH_4^-][NHCl_2]}{[H^-][NH_2Cl]^2}$$

Just as the disinfecting efficiency of solutions of free chlorine will vary with pH because of a change in the HOCl : OCl$^-$ ratio, that of chloramine solutions will vary depending on the $NHCl_2$: NH_2Cl ratio (Fair *et al*, 1948). The disinfection ability of NH_2Cl is high in comparison to the low disinfection ability of $NHCl_2$.

2.1.3. Breakpoint chlorination:

The formation of chloramine and the oxidation of ammonia by chlorine combine to create a unique dose-residual curve for the addition of chlorine to ammonia-containing solutions. Figure 2.2. illustrates this statement.

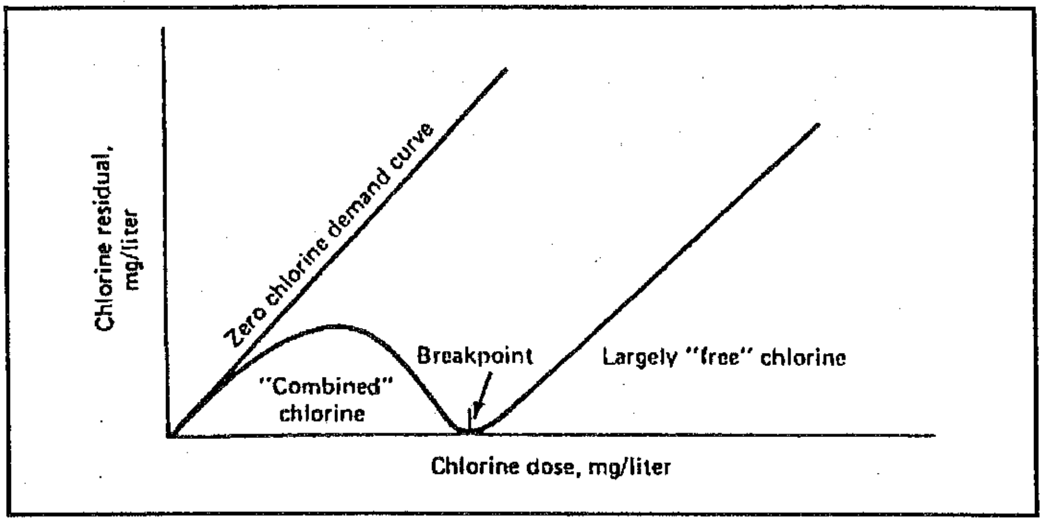

Figure 2.2. A residual-chlorine curve showing a typical breakpoint (Sawyer, McCarty, 1978)

As the chlorine dose increases, the chlorine residual at first rises to a maximum at a $[Cl_2]$ dose to $[NH_3]$ molar ratio of about 1:1. As the chlorine dose is increased further, the chlorine residual falls to a value close to zero. The chlorine dose corresponding to this minimum is called the breakpoint dose depending upon solution conditions. The breakpoint can be observed at a molar ratio of 1.5:1 to 2:1. The primary reaction that causes the residual chlorine concentration to decrease and thus to form the breakpoint is the breakpoint reaction. It can be represented as:

$$2NH_2Cl + HOCl \leftrightarrow N_2 + 3H^+ + 3Cl^- + H_2O$$

or as

$$3HOCl + 2NH_3 \leftrightarrow 3H^+ + 3Cl^- + 3H_2O + N_2$$

These representations account for the observed stoichiometry of 3 moles chlorine per 2 moles of NH_3 (a Cl_2:NH_3 mass ratio of 7.6:1). If the observed stoichiometry is greater than 1.5:1 , the increase in dose can generally be attributed to the formation of some NO_3^- and/or NCl_3 (White, 1992).

Up to a chlorine to ammonia weight ratio of 5:1, the predominant product formed is monochloramine. On the declining side of the curve the monochloramine disappears by forming nitrogen gas or a trace of dichloramine (Montgomery, 1985).

Examining the nature of the chlorine residual present prior to the breakpoint reveals that it is composed almost entirely of chloramines. The chloramines are referred to as "combined chlorine residuals" as opposed to Cl_2, OCl^- and HOCl which are collectively known as "free chlorine residuals".

As the chlorine dose is increased in excess of that required to produce the breakpoint, the increase in residual chlorine will be approximately equal to the excess. The chlorine residual after the breakpoint consists largely of free chlorine with some combined chlorine (White, 1992).

A more detailed examination of the types of chlorine residual would produce Figure 2.3.

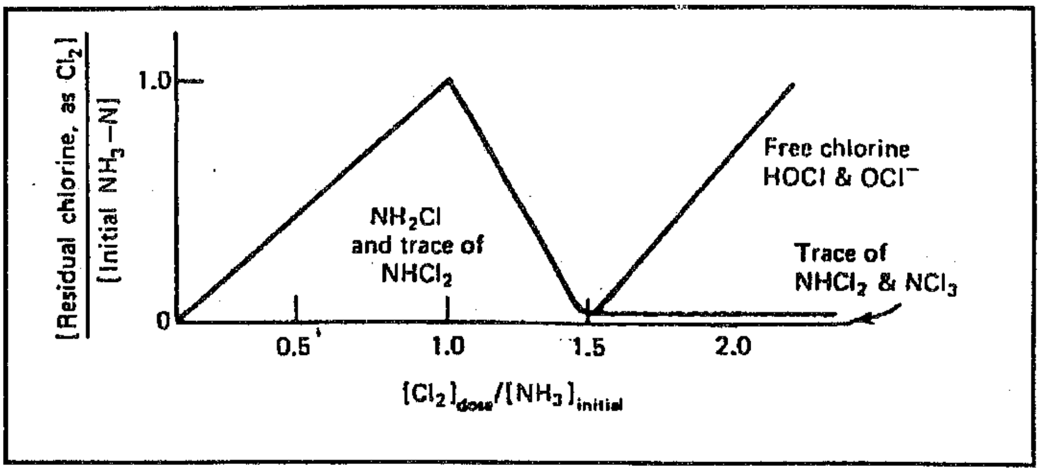

Figure 2.3. Chlorine residual as a function of chlorine dose/initial ammonia ratio at near-neutral pH (White, 1992)

2.1.4. Kinetics of chlorine disinfection:

In most disinfection operations, the destruction of micro-organisms is a gradual process that involves a series of physical, chemical and biochemical steps. Various disinfection models have been proposed based on laboratory data and refined with field data in an effort to predict the outcome of disinfection (Montgomery, 1985).

Although a great deal of work has recently been done on modelling disinfection processes, the main theory of disinfection used today is still the Chick or Chick-Watson disinfection model. This law expresses the rate of micro-organism destruction by the relationship of a first-order chemical reaction:

$$\ln\frac{N}{N_0} = -kt \qquad (2.5)$$

where:

N = number of organisms present at time t

N_0 = number of organisms present at time 0

k = rate constant characteristic of the type of disinfectant

t = time

Unfortunately, the Chick-Watson model is of limited use in most practical disinfection processes. The rate of kill, generally, does not remain constant. It rather increases or decreases with time depending on the type of micro-organism, the varying concentration or the form of disinfectant used, as well as other operating conditions (Montgomery, 1985).

Typical shapes of the disinfection curves that occur during disinfection operations are shown in Figure 2.4. Curve A represents an increase in the rate of kill over most of the contact time. Curves of this kind are also common in disinfection of coliform with chloramines and chlorine dioxide.

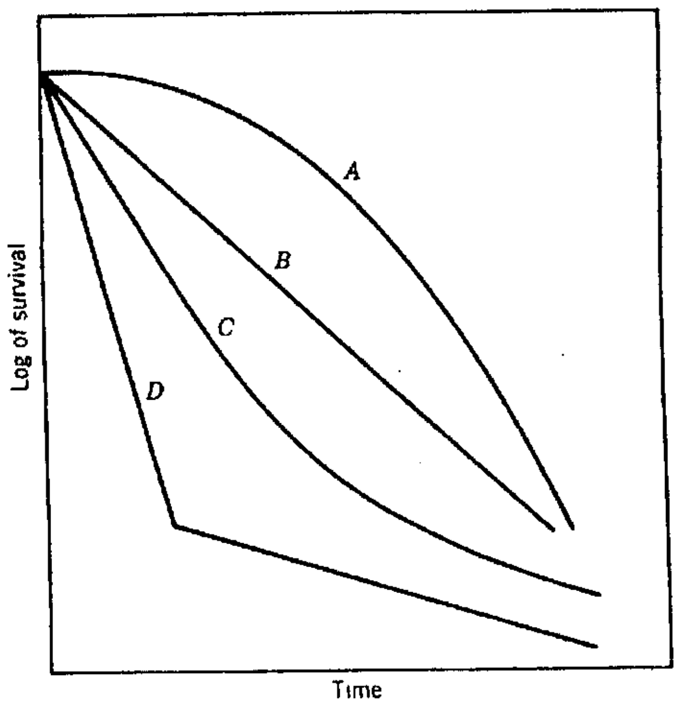

Figure 2.4. Types of survival curves (Montgomery, 1985)

Curve B, described by Chick's law, indicates a constant rate of kill. Curve C, with a decreasing rate of kill with time, is also common in chlorination. Curve D has two steps, each following a different pattern of killing.

In water or wastewater chlorination, an initial lag time normally exists before the disinfection process begins. Possible explanations have been offered by Montgomery (1985) for this initial lag. These explanations are:

(a) It may represent the time required for disinfectant diffusion to and transport across the cell membrane and for the reaction with vital constituents.

(b) Random collisions between molecules of a disinfectant and micro-organisms may be expressed as a Poisson probability. Because organisms may exist in clumps of various sizes, the probability of collision would be based on a multi-Poisson distribution.

Another common feature observed in disinfection data is a decreasing rate of disinfection with time. Several hypotheses have been formulated by Montgomery (1985) to explain the decrease in the rate of kill with time:

(a) A decrease in the germicidal properties of the disinfecting agent with time is evident.

(b) The micro-organisms have a natural heterogeneity in size and resistance to the disinfectant.

(c) An increased resistance to the disinfecting agent is included by exposure of the organisms to this agent.

2.2. Chlorine decay in potable water pipeline systems:

Chemical kinetics is concerned with the rate of reactions. Many reactions have rates which at a given temperature are proportional to the concentration of one, two or more of the reactants raised to a small integral power (Sawyer, McCarty, 1978).

If a reaction is considered in which A, B and C are possible reactants, then the rate equations which express the concentration dependence of the reaction rate may take one of the following forms:

Rate = kC_a	1st order
Rate = kC_a^2 or kC_aC_b	2nd order
Rate = kC_a^3 or $kC_a^2C_b$ or $kC_aC_bC_c$	3rd order

where C_a, C_b and C_c represent the concentrations of reactants A, B and C respectively (Sawyer, McCarty, 1978).

2.2.1. First order decay:

The first-order kinetic model for the disappearance of residual chlorine due to reactions with materials in the aqueous phase at different residence times in the network may be expressed as:

$$\frac{dC}{dt} = -kC \qquad (2.6)$$

where:

C = residual chlorine concentration (mg/l)

k = first-order decay rate constant (1/h)

The residence time is defined as the pipe length divided by the mean flow velocity in the pipe (Sawyer, McCarty, 1978).

By integrating equation (2.6) the general first-order decay rate equation can be obtained:

$$C(t) = C_0 e^{-kt} \tag{2.7}$$

where:

$C(t)$ = chlorine concentration at time t (mg/l)
C_0 = initial chlorine concentration (mg/l)
t = residence time in the pipe

The chlorine decay rate constant k is site specific and must be verified by field measurements (Vasconcelos *et al*, 1995).

2.2.2. Second order decay:

The second-order decay rate process may be expressed as:

$$\frac{dC}{dt} = -k' C^2 \tag{2.8}$$

By integrating equation (2.8) the equation to determine the concentration at a specific time can be obtained:

$$C(t) = \frac{C_0}{1 + C_0 k' t} \tag{2.9}$$

where:

k' = a second-order decay rate constant (Vasconcelos *et al*, 1995)

2.2.3. n^{th}-order decay:

The n^{th}-order decay rate process is described as:

$$\frac{dC}{dt} = -k\,C^{n} \tag{2.10}$$

By integrating equation (2.10) an equation can be obtained to determine the chlorine concentration at any time in the distribution system:

$$C(t) = \left[(kt)(n-1) + \left(\frac{1}{C_o}\right)^{(n-1)}\right]^{\left(\frac{-1}{n-1}\right)} \tag{2.11}$$

where:

k = a n^{th}-order decay rate constant (Vasconcelos *et al*, 1995)

2.2.4. Factors affecting chlorine decay in distribution systems:

(a) Pipelines:

Besides the reaction rate order just described, chlorine decay in single pipelines is also affected by other parameters, i.e. the radial diffusion in the water, the influence of the pipe wall on the decay rate as well as the reaction that takes place in the bulk water phase - these factors were earlier enumerated in section 1.1. The modelling of chlorine decay in a single pipeline therefore requires a number of inputs, of which very few have been explicitly verified.

(b) Networks:

Since a network consists of different pipelines with different nodes incorporated in the network it is even more difficult to model chlorine decay in such a network. Not every pipe in the network has the same residence time, therefore a complete study is necessary for each pipe in the system. Dead ends of pipelines obviously greatly affect the chlorine decay in the network. Despite all the problems associated with single pipes, a further two debatable assumptions need to be mentioned:

(a) Full blending at each node in the network is assumed. This might be true for two pipes crossing at a single point. Where two pipes cross a single third pipe from opposite directions this statement is not convincing.

(b) It is also assumed that all the pipes in a network act in the same way. This statement does not allow for different wall coatings, pipe diameter and reduced or increased flow velocity in certain pipes.

It is therefore evident that a thorough study of a single pipe be completed before a network can be modelled.

2.2.5. Previous research and results:

(a) American Water Works Association Research Foundation (AWWARF):

A study completed on the topic of chlorine decay in distribution systems (Vasconcelos *et al*, 1995) proved to be very useful in this study. The study was done during 1993/94 by the following participants under sponsorship of AWWARF.

- Montgomery Watson, Americas, Pasadena, California
- Lyonnaise des Eaux, Centre International de Recherche sur l'Eau et l'Environnement (CIRSEE), Le Pecq, France
- University of Cincinnati, Department of Civil and Environmental Engineering, Cincinnati, Ohio
- U.S. Environmental Protection Agency, Drinking Water Research Division, RREL, Cincinnati, Ohio
- Walter M. Grayman, Consulting Engineer, Cincinnati, Ohio

Tests on 11 different waters formed the database on which the results were based. For each water, a non-linear least squares regression procedure was used to fit the integrated forms of the bulk reaction models to the data collected. The study tested raw source water obtained from the participating utilities listed below. These utilities were selected in order to examine a wide range of source water qualities and to include systems having, where possible, small isolated zones or long isolated lines to minimise the number of samples required.

- City of Bellingham, Washington
- General Waterworks Corporation, Harrisburg, Pennsylvania
- City of Fairfield, California
- North Marin Water District, Novato, California
- North Penn Water Authority, Lansdale, Pennsylvania
- Parisienne Des Eaux, Paris, France.

The main objectives of the study were:

1. To establish protocols for sampling of distribution systems to obtain data for calibrating predictive models of chlorine decay.
2. To evaluate alternative kinetic models for chlorine decay in distribution systems using data collected from field sampling studies.

3. To develop better understanding of the factors influencing the reactivity of chlorine in the pipe environment.
4. To make available to the water industry the results of these investigations for use in system operations and in planning similar water quality studies.

To fully understand the scope and findings of this study, background information is necessary. In the United States of America a minimum chlorine residual level of 0.2 mg/l at the entrance to the distribution system along with the preservation of a detectable residual level throughout the system are currently required by the Surface Water Treatment Rule (SWTR).

Several models have been analysed to obtain the best mathematical solution to measure and predict chlorine decay in distribution systems. These models with a short description of each are presented below:

1. *First order decay* - in the first order decay model the rate of decay is proportional to the concentration of chlorine remaining (This model is described in detail in Chapter 3, sections 3.3.3 and 3.4.3 of this dissertation).
2. *Power law decay (n^th order)* - in the n^th order decay model the rate of decay is proportional to the concentration remaining raised to the n^th power (This model is described in detail in Chapter 3, sections 3.3.4 and 3.4.4 of this dissertation).
3. *First order decay with stable component* - in the first order decay model with stable component the chlorine decay follows first order kinetics until a limiting concentration is reached (This model is described in detail in Chapter 5, section 5.3.1 of this dissertation).
4. *Power law decay with stable component (n^th order)* - in the power law decay model with stable component the decay follows n^th order decay again until a limiting concentration is reached.

5. *Parallel first order decay* - in the parallel first order decay model, a fixed proportion of the chlorine follows a rapid first order decay while the remaining proportion decays at a slower first order rate.

A number of significant findings have emerged from this study by AWWARF which increase our understanding of the mechanisms of chlorine decay and the kinetic models which describe it. The major findings are listed below:

1. Chlorine decay in distribution systems can occur due to reactions both within the bulk fluid and from reactions with materials associated with the pipe wall.
2. Analyses of chlorine decay tests in bottles conducted on a variety of waters in the USA showed that n^{th}-order or parallel first order kinetic models provided better fits to the data than did first order models. In about half the cases, the n^{th}-order model provided a best fit while the parallel first order model was best for the other half. However, there is no evidence in the literature that the parallel first order model has actually been applied to water distribution systems. The commonly assumed first order model did not best describe any of these waters, however the differences between the model fits were not very large in most cases.
3. Laboratory studies showed that pipe wall reactions related to corrosion of ferrous pipe materials can consume significantly more chlorine than those related to biofilm.
4. The rate of reaction of chlorine at the pipe wall is inversely related to pipe diameter and can be limited by the rate of mass transfer of chlorine to the wall.
5. There is currently no established method for directly determining the kinetics of chlorine decay due to pipe wall reactions - calibration against field data must be used instead.

6. Mass transfer expressions based on a two dimensional model containing radial diffusion can produce more accurate results than those using a lumped mass transfer coefficient, but are less suitable for inclusion in network models applied to large systems.
7. A well calibrated hydraulic model, preferably one based on tracer studies, is a prerequisite for attempting the modelling of water quality in a distribution system.
8. Calibration of network chlorine decay models can be based on using a first order kinetic constant for bulk reactions derived from bottle tests and either first or zero order kinetics for wall reactions, where the wall kinetic constant is inversely related to pipe roughness coefficient.

(b) Chambers *et al*:

A study was recently done by Chambers *et al* on two distribution systems in the United Kingdom (Chambers *et al*, 1995).

The aim of the study was to test the validity of the first order exponential decay expression for free and total chlorine modelling. The software packages WATNET and WATQUAL were used to model the two distribution systems of similar characteristics (similar water, mains material and age). The main difference between the systems was that one network model was significantly more detailed than the other.

It was found in the study that a simplified first order exponential decay expression to model reactive substances in distribution systems can adequately model the decay seen in distribution systems.

The water quality models required calibration. A distribution sampling programme was devised to collect appropriate chlorine decay information to enable calibration of the models. Experiments on the water alone only determined the chlorine decay rate for the water and this was not representative of decay in the distribution system. The decay found in distribution proved to be higher than that obtained in laboratory tests. Mean values for the two networks are summarised in Table 2.2.

Table 2.2. Decay rate values obtained in the study by Chambers *et al*, 1995

Network	**Mean decay rate value for field sampling tests**		**Mean decay rate value for laboratory tests**	
	Free Cl_2	**Total Cl_2**	**Free Cl_2**	**Total Cl_2**
	(per hour)	(per hour)	(per hour)	(per hour)
A	0.29	0.14	0.03	0.04
B	0.29	0.17	0.21	0.12

In order to ensure that the models accurately reproduced the transit times in the network, flow measurements were also recorded. Once gathered, the data were used to calculate network-wide rate constants for free and total chlorine. Rate constants for specific areas or individual pipes were not justified for the two networks studied but this may not be true for other systems. The rate constants for the two networks studied during the project were similar.

The results showed that the exponential first order decay model is appropriate for modelling chlorine residuals in distribution. However, no study was conducted on the n^{th}-order decay rate model.

The project revealed several important points to consider when modelling chlorine residuals in distribution. It should be borne in mind that a network model used for the simulation of chlorine residuals may need to be highly detailed. Consequently, special attention should be paid to the modelling of demands. The success of water quality modelling is dependent on a well calibrated hydraulic model. When calibrating chlorine decay it is important to ensure that the chlorine concentration at the input to distribution are monitored for a sufficiently long period to allow correlation with the chlorine concentrations measured in distribution. Finally, the study by Chambers *et al* has shown that it is possible to produce water quality models which give useful results.

2.2.6. Conclusions from literature review:

From the literature reviewed, the following conclusions can be drawn which are pertinent to this study:

- Both free chlorine and monochloramine can be used as disinfectants that produce residual chlorine. The chlorine decay studies reviewed only the decay and modelling of free chlorine in distribution systems, with no attention given to the decay of monochloramine.
- A variety of mathematical models can be used to describe the decay of chlorine in bulk solutions. Although first order decay is commonly adopted as the simplest, easiest model, there are indications that better descriptions are obtained by using more elaborate models, e.g. n^{th}-order decay.
- The previous studies concur that the pipe wall does increase the chlorine demand beyond that measured for bulk solutions, but very little clear conclusions can be drawn from the scant data reported.
- The data reported from the previous studies are from regions where:
  (a) a higher level of treatment is generally practised
  (b) colder temperatures are encountered
  (c) lower levels of organic carbon (less eutrophic) would be expected than in typical South African surface water sources.

It would be useful to test the previous findings under USA on local conditions, and to extend the work to include free chlorine and monochloramine.

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CHAPTER 3

MATHEMATICAL MODELLING OF CHLORINE DECAY IN A SINGLE WATER PIPELINE

3.1. Introduction:

This chapter deals with the various mathematical models available to the water industry for modelling chlorine decay in distribution systems.

Several models are presented, each with it's own description:

- First order, three parameter model
- First order, two parameter model
- First order, one parameter model
- n^{th}-order, one parameter model

It is necessary to pause for a moment to consider each of these mathematical models, and how they can be applied to water flow in a pipe.

3.2. Mathematical models for the determination of chlorine concentration decay:

From the foregoing chapters, it is clear that two aspects of chlorine modelling in pipelines are still open to debate:

(a) The reaction order of chlorine decay in the bulk liquid phase (first order vs n^{th}-order)

(b) The number of parameters considered when modelling pipelines (bulk water flow, pipe wall reactions and radial diffusion from the bulk water flow to the pipe wall)

In this chapter, a theoretical development will be presented to show how a combination of assumptions can be used to derive the corresponding mathematical equations. Table 3.1 is presented to guide the reader through the rest of this chapter.

Table 3.1. Differences between the various mathematical models

Reaction order	Number of parameters	Parameters concerned	Comments (See section)
First-order	3 parameters	Bulk water flow	3.3.1.
		Pipe wall	
		Radial diffusion	
	2 parameters	Bulk water flow	3.3.2. & 3.4.1.
		Pipe wall	
	1 parameter	Bulk water flow	3.3.3. & 3.4.2.
n^{th}-order	3 parameters	Bulk water flow	not presented
		Pipe wall	
		Radial diffusion	
	2 parameters	Bulk water flow	not presented
		Pipe wall	
	1 parameter	Bulk water flow	3.3.4. & 3.4.3.

3.3. Qualitative description of the loss models:

3.3.1. First-order, three parameter model:

The first-order, three parameter loss model firstly accounts for the chlorine concentration in the **bulk liquid phase**. The residence time is computed by dividing the pipe length by the average flow velocity in the pipe. By performing measurements in the distribution system, researchers have calculated the decay rate constant, k, for site specific tests.

The chlorine concentration in the water is secondly influenced by the reaction of the **pipe wall** with the water flowing past it. Biofilms exist on the pipe wall and contribute to chlorine decay in distribution systems. Three different wall conditions can be considered in the derivation of the mathematical model:

(a) Perfect sink
(b) No consumption at the wall
(c) Partial consumption at the wall

A third factor that contributes to chlorine decay is the transportation of the chlorine from the bulk liquid phase to the vicinity of the biofilm at the pipe walls. It is an important factor in understanding chlorine decay rates. Higher disinfectant concentrations are required to inactivate bacterial populations in the biofilm as compared to those suspended in the bulk liquid phase. It is therefore important that the transport of chlorine to the pipe wall is not inhibited by inadequate **radial diffusion**.

3.3.2. First-order, two parameter model:

In this case the parameters concerned are the bulk liquid phase and the influence of the pipe wall on the chlorine concentration decay. The effect of radial diffusion in a pipe is ignored with the implicit assumption that radial diffusion is not the rate-limiting parameter. This enables us to make use of a simplified equation for the determination of the chlorine concentration at any point concerned in the pipe.

3.3.3. First-order, one parameter model:

This model comprises of only one parameter - probably the most important of them all, namely the bulk water in the pipeline. It is the most simplified of all models and accounts only for the decay in chlorine concentration in the bulk liquid phase. The influence of the pipe wall, and radial diffusion are ignored.

The importance of the pipe wall can be established by comparing chlorine decay in an actual pipeline with a batch system. If the chlorine decay is more rapid in the pipeline than in a batch system, the difference could be attributed to the effect of the pipe wall. If this difference is significant, it would be more appropriate to use a two-parameter, or even a three-parameter model.

3.3.4. nth-order, one parameter model:

The nth-order model can be described in exactly the same manner as the first-order, one parameter model except that the reaction rate is of the nth-order. In other words the assumption of a reaction rate of $k = 1$ is not made. The reaction rate is calculated from laboratory measurements of chlorine loss in a batch system.

3.4. Derivation of the various mathematical models:

3.4.1. First-order, two parameter model:

The two parameter mathematical model, as the other models, provides a mechanism for considering the loss of chlorine concentration by reaction as it travels through the distribution system. Reaction can occur both within the bulk flow and with material along the pipe wall.

In general, within any given pipe, material in the bulk flow will decrease at a rate equal to (Rossman, 1994):

$$\theta(c) = -k_b c - \frac{k_f}{R_H}(c - c_w) \tag{3.1}$$

where:

k_b = first-order bulk reaction rate constant (1/s)
c = chlorine concentration in bulk flow (mg/l)
k_f = mass transfer coefficient between bulk flow and pipe wall (m/s)
R_H = hydraulic radius of pipe (m) [= pipe radius/2]
c_w = chlorine concentration at the wall (mg/l)

The first term in equation (3.1) models bulk flow reaction while the second term, which includes a new unknown, c_w, represents the rate at which material is transported between the bulk flow and reaction sites on the pipe wall. Assuming that the rate of reaction at the wall is first order with respect to c_w and that it proceeds at the same rate as material is transported at the wall (so that no accumulation occurs), we can write the following mass balance for the wall reaction:

$$k_f c - k_f c_w = k_w c_w \tag{3.2}$$

where k_w is a wall reaction rate constant.

Solving for c_w yields:

$$
\begin{aligned}
& k_f c - k_f c_w = k_w c_w \\
\therefore\ & k_f c = k_w c_w + k_f c_w \\
\therefore\ & k_f c = c_w\left(k_w + k_f\right) \\
\therefore\ & c_w = \frac{k_f c}{\left(k_w + k_f\right)}
\end{aligned}
\tag{3.3}
$$

Substituting equation (3.3) into equation (3.1) results in the following reaction rate expression:

$$
\begin{aligned}
& \theta(c) = -k_b c - \frac{k_f}{R_H}\left(c - \frac{k_f c}{\left(k_w + k_f\right)}\right) \\
\therefore\ & \theta(c) = -k_b c - \frac{k_f c}{R_H}\left(1 - \frac{k_f}{\left(k_w + k_f\right)}\right) \\
\therefore\ & \theta(c) = -k_b c - \frac{k_f c}{R_H}\left(\frac{k_w}{k_w + k_f}\right) \\
\therefore\ & \theta(c) = -k_b c - \frac{k_w k_f c}{R_H\left(k_w + k_f\right)} \\
\therefore\ & \theta(c) = -K.c
\end{aligned}
\tag{3.4}
$$

where K is an overall first-order rate constant equal to $k_b + \dfrac{k_w k_f}{R_H\left(k_w + k_f\right)}$.

The mass transfer coefficient, k_f, can be calculated using the dimensionless Sherwood number as follows (Rossman, 1994):

$$k_f = \frac{Sh.D}{d}$$

$$Sh = 0.023\,Re^{0.83}Sc^{0.333} \quad \text{for } Re \geq 2300 \tag{3.5}$$

$$Sh = 3.65 + \frac{0.0668\left(\frac{d}{L}\right)Re.Sc}{1+0.04\left[\left(\frac{d}{L}\right)Re.Sc\right]^{0.67}} \quad \text{for } Re < 2300 \tag{3.6}$$

where:

k_f = mass transfer coefficient

Sh = Sherwood number

Re = Reynolds number [= $qd/(A\nu)$]

Sc = Schmidt number [= ν/D]

d = pipe diameter (m)

L = pipe length (m)

q = flow rate (m^3/s)

A = cross-sectional flow area of the pipe (m^2)

D = molecular diffusivity of chlorine in water (m^2/s)

ν = kinematic viscosity of water (m^2/s)

Equation (3.5) applies to turbulent flow where the mass transfer coefficient is independent of the position along the pipe. For laminar flow, equation (3.6) supplies an average value of the mass transfer coefficient along the length of the pipe.

3.4.2. First-order, one parameter model:

The first-order, one parameter chlorine reduction model can be represented as:

$$\frac{dC}{dt} = -kC$$

$$\therefore \frac{dC}{C} = -k\,dt$$

$$\therefore \int_{C_0}^{C} \frac{dC}{C} = -k\int_{0}^{t} dt$$

(cont.)

$$\therefore \ln C - \ln C_0 = -kt$$

$$\therefore \ln \frac{C}{C_0} = -kt$$

$$\therefore C(t) = C_0\, e^{-kt} \tag{3.7}$$

where:

$C(t)$ = chlorine concentration at time t (mg/l)

C_0 = initial chlorine concentration (mg/l)

k = first-order chlorine decay rate constant (1/s)

t = residence time in the pipe

By using this equation the chlorine concentration at any point at time t can be calculated in the pipe.

3.4.3. n

Equation (3.8) describes the reduction of chlorine concentration for the nth-order case. By integration, equation (3.9) is obtained by which the concentration at any point in the pipe can be calculated.

$$\frac{dC}{dt} = -kC^n \tag{3.8}$$

$$\therefore \frac{dC}{C^n} = -k\,dt$$

$$\therefore \int_{C_0}^{C} \frac{dC}{C^n} = -k \int_0^t dt$$

$$\therefore \left[\frac{C^{(-n+1)}}{-n+1}\right] - \left[\frac{C_0^{(-n+1)}}{-n+1}\right] = -kt$$

$$\therefore C^{(-n+1)} - C_0^{(-n+1)} = -kt(-n+1)$$

$$\therefore C = \left[kt(n-1) + C_0^{(-n+1)}\right]^{\left(\frac{1}{-n+1}\right)} \qquad \text{(cont.)}$$

$$\therefore C = \left[kt(n-1) + C_0^{(-n+1)}\right]^{\left(\frac{1}{-n+1}\right)}$$

$$\therefore C = \left[kt(n-1) + \frac{1}{C_0}^{-(-n+1)}\right]^{\left(\frac{1}{-n+1}\right)}$$

$$\therefore C = \left[kt(n-1) + \frac{1}{C_0}^{(n-1)}\right]^{\left(-\frac{1}{n-1}\right)} \tag{3.9}$$

where:

$C(t)$ = chlorine concentration at time t (mg/l)

C_0 = initial chlorine concentration (mg/l)

k = nth-order chlorine decay rate constant (1/s)

t = residence time in the pipe

n = order coefficient

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CHAPTER 4

MATERIALS AND METHODS

4.1. Water sources tested:

The experimental work in this study was executed on four different water sources, i.e. Vaal Dam (Rand Water), Barrage, Rietvlei Dam, and secondary effluent from the Leeuwkop wastewater treatment plant in Vereeniging. The reason for the use of these water sources was to test the best and worst sources available to obtain results over the full spectrum of available water sources.

The points where the water samples were taken are as follow:

(a) In the case of Vaal Dam water, the samples were taken at the filter house before the water was treated with chlorine.

(b) Rietvlei Dam water was sampled at the inlet box of the adjacent water treatment plant

(c) Water samples from the Barrage were again taken just before chlorination was due to take place.

(d) The water samples from the Leeuwkop wastewater treatment plant were taken after complete purification had taken place - just before the outlet from the treatment plant.

In all cases filtered water were used for experimental tests.

4.1.1. Laboratory batch tests:

To bring the whole project in line with the objectives of the study, laboratory batch tests were necessary to determine the decay rate constants and reaction orders of the different water types.

An accurate estimate of the chlorine decay rate constants for the different water types was necessary to predict chlorine decay in pipelines. To do this it was vital that laboratory tests were conducted first to determine the reaction order and decay rate constants of the different water types.

In order to test the different waters in the laboratory several solutions were necessary to obtain free and total chlorine residuals. The preparation of the phosphate buffer solution, N,N-diethyl-p-phenylenediamine (DPD) indicator solution, standard ferrous ammonium sulphate (FAS) titrant and the potassium iodide solution is described in section 4.2.4 (APHA *et al*, 1985).

4.1.2. Pipeline tests:

Different Rand Water pipeline sections were selected (discussed in Chapter 6) to test for free and combined chlorine residuals as well as to determine the chlorine decay rate constant. To determine the chlorine decay in the pipeline it was necessary to measure the chlorine concentration frequently at the inlet and outlet as well as at predetermined intervals between the inlet and the outlet of the pipe as to determine the profile of the chlorine decay throughout the pipe.

4.1.3. Frequency of testing:

In the case of free chlorine and combined chlorine, laboratory experiments tests were conducted on four occasions. The first round of tests was done for a total period of 48 hours (measurements were taken on the hour, every hour) to enable us to develop standardised procedures for testing free chlorine decay as well as monochloramine decay. After this procedure was in place the remaining experimental tests were conducted during October 1995, November 1995 and January 1996. During these experimental periods the water samples were tested on the hour for a total time period as stated in Chapter 5.

The pipeline experiments were conducted in conjunction with the laboratory batch tests i.e. also three rounds of identical tests at different times. Again the developed standardised procedures were used as basis on which these pipeline tests were conducted.

4.2. Analytical procedures and reagents:

4.2.1. Chlorine dosing:

A chlorine solution was prepared with an initial concentration of 200 mg/l to ensure that the volume of the 100 ml water samples needed to test for free and combined chlorine residuals was not increased by more than 5% on addition of the chlorine solution.

Each water sample was treated with a known volume of the chlorine solution to ensure that enough residual chlorine would be present to conduct the tests over desired period of time.

4.2.2. The DPD ferrous titrimetric method for the determination of free and combined chlorine residuals:

The DPD Ferrous titrimetric method for the determination of free and combined chlorine residuals in water is described below in accordance with *Standard Methods for the examination of water and wastewater, 16th edition* (APHA *et al*, 1985).

(a) Principle:

N,N-diethyl-p-phenylenediamine (DPD) is used as an indicator in the titrimetric procedure with ferrous ammonium sulphate (FAS). In the absence of iodide ion, free chlorine reacts instantly with DPD indicator to produce a red colour. Subsequent addition of a small amount of iodide ion acts catalytically to cause monochloramine to produce colour. Addition of iodide ion to excess evokes a rapid response from dichloramine. In the presence of iodide ion, part of the nitrogen trichloride (NCl_3) is included with dichloramine and part with free chlorine.

For accurate results careful pH control is essential. In this method it is controlled with the addition of the phosphate buffer. At the proper pH of 6.2 to 6.5, the red colours produced may be titrated to sharp colourless end points. Titrate as soon as the red colour is formed in each step. Too low a pH in the first step tends to make the monochloramine show in the free-chlorine step and the dichloramine in the monochloramine step. Too high a pH causes dissolved oxygen to give a colour.

In all methods for differentiating free chlorine from chloramine, higher temperatures increase the tendency for chloramines to react and lead to increased apparent free-chlorine results. Higher temperatures also increase colour fading. Complete measurements rapidly, especially at a higher temperature.

During this study different temperatures were used to conduct experiments. Water samples were placed in incubators to reach temperatures of 10°C, 15°C and 27°C.

(b) Procedure:

The quantities below are suitable for concentrations of total chlorine up to 5 mg/l. If total chlorine exceeds 5 mg/l, use a smaller sample and dilute to a total volume of 100 ml. Mix usual volumes of buffer reagent and DPD indicator solution with distilled water *before* adding sufficient sample to bring total volume to 100 ml. *(If sample is added before buffer, the test does not work.)*

Free chlorine or chloramine:

Place 5 ml each of buffer reagent and DPD indicator solution in a titration flask and mix (or use about 500 mg DPD powder). Add 100 ml sample, or diluted sample, and mix.

Free chlorine:

Titrate rapidly with standard FAS titrant until red colour is discharged (Reading A)

Monochloramine:

Add one very small crystal of KI (about 0.5 g) or 0.1 ml (2 drops) KI solution and mix. Continue titration until red colour is discharged again (Reading B)

Dichloramine:

Add several crystals KI (about 1 g) and mix to dissolve. Leave for two minutes and continue titrating until red colour is discharged (Reading C). For dichloramine concentrations greater than 1 mg/l, leave two minutes more if colour driftback indicates a slightly incomplete reaction.

Simplified procedure for free and combined chlorine or total chlorine:

Omit the procedure for monochloramine discussed above to obtain monochloramine and dichloramine together as combined chlorine. To obtain total chlorine in one reading, add full amount of KI at the start, with the specified amounts of buffer reagent and DPD indicator, and titrate after two minutes standing.

Nitrogen trichloride:

Place one very small crystal of KI (about 0.5 mg) or 0.1 ml KI solution in a titration flask. Add 100 ml sample and mix. Add contents to a second flask containing 5 ml each of buffer reagent and DPD indicator solution (or add about 500 mg DPD powder direct to the first flask). Titrate rapidly with standard FAS titrant until red colour is discharged (Reading N).

(c) Calculation:

For a 100 ml sample, 1 ml standard FAS titrant = 1 mg Cl as Cl_2/l.

In the event that monochloramine is present with NCl_3, it will be included in N, in which case NCl_3 is obtained from 2(N - B).

Table 4.1. Formula table for the calculation of the different chlorine species

Reading	NCl_3 absent	NCl_3 present
A	Free Cl	Free Cl
B - A	NH_2Cl	NH_2Cl
C - B	$NHCl_2$	$NHCl_2 + \frac{1}{2}NCl_3$
N	-	Free Cl + $\frac{1}{2}NCl_3$
2(N - A)	-	NCl_3
C - N	-	$NHCl_2$

4.2.3. Reagents:

(a) Phosphate buffer solution:

Dissolve 24 g anhydrous Na_2HPO_4 and 46 g anhydrous KH_2PO_4 in distilled water. Combine with 100 ml distilled water in which 800 mg disodium ethylenediamine tetraacetate dihydrate (EDTA) have been dissolved. Dilute to 1 l with distilled water and add 20 mg $HgCl_2$ to prevent mold growth and interference in the free chlorine test caused by any trace amounts of iodide in the reagents.

(b) N,N-Diethyl-p-phenylenediamine (DPD) indicator solution:

Dissolve 1 g DPD oxalate, or 1.5 g DPD sulphate pentahydrate, or 1.1 g anhydrous DPD sulphate in chlorine-free distilled water containing 8 ml 1 + 3 H_2SO_4 and 200 mg disodium EDTA. Make up to 1 l, store in a brown glass-stoppered bottle in the dark and discard when coloured.

(c) Standard ferrous ammonium sulphate (FAS) titrant:

Dissolve 1.106 g $Fe(NH_4)_2(SO_4)_2 \bullet 6H_2O$ in distilled water containing 1 ml 1 + 3 H_2SO_4 and make up to 1 l with freshly boiled and cooled distilled water.

(d) Potassium iodide, KI, crystals.

(e) Potassium iodide solution:

Dissolve 500 mg KI and dilute to 100 ml, using freshly boiled and cooled distilled water. Store in a brown glass-stoppered bottle.

4.3. Determination of the breakpoint:

The chlorine demand of a water is the difference between the amount of free chlorine applied and the amount of free chlorine remaining at the end of the contact period.

The chlorine demand is different with different waters, and even with a given water will vary with the amount of chlorine applied, the desired residual, time of contact, pH and temperature. The test should be conducted with chlorine or with hypochlorites, depending upon the form that will be used in practice.

In preparing the samples to test for breakpoint-chlorination in this study, 5 ml of the phosphate buffer solution was mixed with 100 ml of the sampled water in an Erlenmeyer flask. Thereafter, known but varying volumes of the chlorine solution (up to a chlorine concentration of 10 mg/l) were added to the flask at predetermined time intervals to permit reasonable contact times and enough time for testing the water samples. After the addition of the chlorine solution each sample was closed and placed in the dark to prevent chlorine decay by other factors than the water itself. On the expiring of the 20 minute contact time, 5 ml of the DPD-indicator solution was added to produce a red colour. Thereafter the sample was titrated with the FAS-titrant in order to determine the free and combined chlorine residuals.

Measurement of chlorine demand can be readily made by treating a series of samples of the water in question with known but varying dosages of chlorine or hypochlorite. The water samples should be at a temperature within the range of interest, and after the desired contact period, determination of residual chlorine in the samples will demonstrate which dosage satisfied the requirements of the chlorine demand, in terms of the desired residual.

4.3.1. General procedure for the determination of the breakpoint:

Measure at least 10 equal sample portions, preferably into brown, glass-stoppered bottles or Erlenmeyer flasks of ample capacity to permit mixing.

Add an amount of chlorine to the first portion that leaves no chlorine residual at the end of the contact period. Add increasing amounts of chlorine to successive portions in the series. Increase the dosage between portions in increments of 0.1 mg/l for determining low demands and up to 1 mg/l or more for higher demands. Mix while adding. Dose sample portions according to a staggered schedule that will permit determining chlorine residual at predetermined contact times. At the end of the contact period, determine the free and/or combined chlorine residual by the method described in section 4.2.2.

4.4. Measurement of chlorine decay:

Water samples were collected from the different sampling points and stored in dark, airtight containers. Each sample were then treated with a known volume of the chlorine solution after the breakpoint of the water was known. Contact times of up to 48 hours were used. After the desired time period elapsed, the water sample was tested to determine the residual chlorine in the sample. Samples were tested on the hour, every hour.

This chlorine residual was calculated by adding 5 ml of the phosphate buffer solution to 100 ml of the sampled water. The sample was then treated with 5 ml of the DPD-indicator solution to produce a red colour and titrated with the FAS-titrant to determine the free and combined chlorine residual in the sample.

After all the samples had been tested graphs were drawn by which it was possible to calculate the chlorine decay rate constant for each specific sample - this is covered in detail in the following chapter.

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CHAPTER 5

CHLORINE DECAY BEHAVIOUR IN LABORATORY BATCH TESTS

5.1. Objectives of the laboratory tests:

The objectives of the laboratory tests were:

(a) To develop standard test procedures for both free chlorine and monochloramine by which the chlorine decay could be measured.
(b) To select the most suitable mathematical model for the calculation of chlorine decay.
(c) To measure the effect of temperature on chlorine decay.
(d) To establish typical ranges for the model calibration constants i.e. the decay rate constant, k and the reaction order, n.

5.2. Development of standard test procedures:

5.2.1. Requirements of a practical test procedure:

The to be developed standard test procedures must satisfy the following two requirements:

(a) The standard test procedures must be short enough to be practical
(b) It must however be long enough to be reliable

5.2.2. Free chlorine decay:

(a) Elimination of initial fast reactions.

The first round of experimental work was conducted over a period of 48 hours with an added chlorine concentration of breakpoint + 1 mg/l. The breakpoint was determined after 20 minutes as discussed in Chapter 4. All four water samples were tested for all chlorine species at pre-determined time intervals. The readings were taken on 15 minute intervals for the first half hour, on the first hour and every second hour thereafter for a total time period of 48 hours.

All the data for each water type were graphed over the 48 hour experimental period. Thereafter, several curve fittings were done by applying the least squares method for varying time intervals to produce the best curve fitting for the shortest time possible.

This statement is explained in detail as follows:

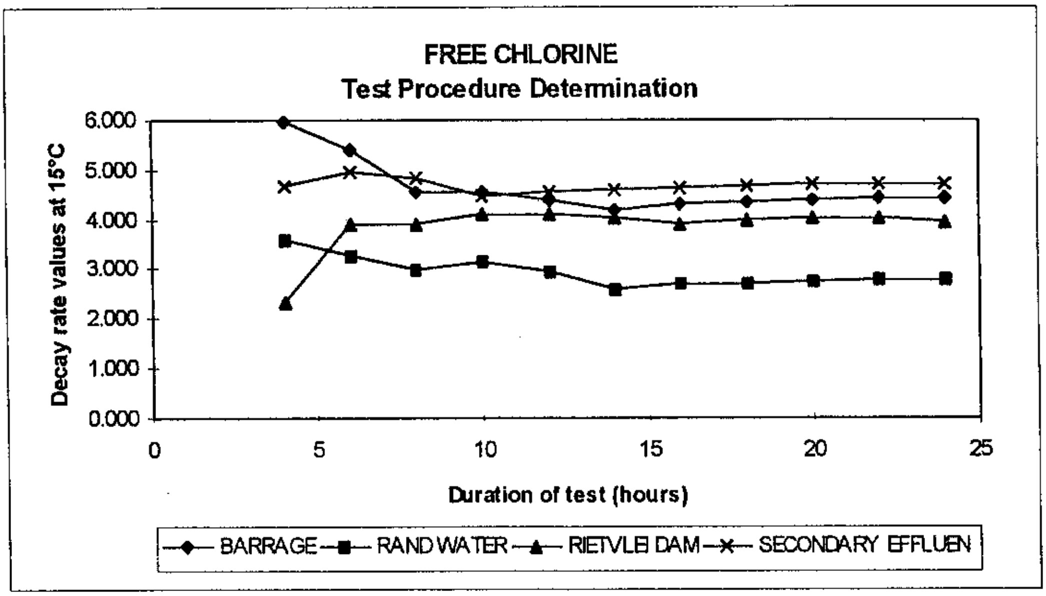
After all the data were graphed, two types of curve fittings were done. Firstly, the initial data point was maintained and curve fittings were done with decreasing time intervals e.g. one curve fitting of 0.25 hour to 48 hours was completed. This was followed by another for the interval 0.25 hour to 46 hours until a fitting for the interval 0.25 hour to 6 hours was reached. Secondly, the final data point was kept constant while the initial point was increased e.g. a curve fitting for the interval 0.25 hour to 48 hours was followed by a fitting for the interval 0.5 hour to 48 hours. This procedure was followed until a curve for the interval 24 hours to 48 hours was reached.

By doing this, it was possible to see the effect of different time intervals on the chlorine decay rate constant. It was evident from these graphs that during the first hour of testing, initial fast reactions took place which did not follow the long-term decay rate. By analysing the graphs it was clear that the testing of samples should not commence within the first hour due to the initial reactions. After an hour the reactions appear to have stabilised.

(b) Minimum test duration:

The graphs mentioned in the previous section were analysed thoroughly. The data showed that the shortest time period in which to conduct laboratory experiments for the determination of the decay rate constant was 8 hours - measured every hour.

Graph 5.1 represents the effect of the test duration on the first order decay rate constant for free chlorine, shown for the four different raw water types. Each data point represents a decay rate constant obtained from the curve fittings mentioned in section (a). It was evident that for time periods of 8 hours or larger the decay rate constants stabilised for all four raw water sources.



Graph 5.1. The effect of the test duration on the first order decay rate constant for free chlorine, shown for the four different raw water sources

(c) Summary of test procedure:

To determine the chlorine decay rate constant for free chlorine, laboratory experiments should be conducted over a total time period of 8 hours. Measurements should be taken every hour. No measurements should be taken during the first hour of experimental tests.

5.2.3. Monochloramine decay:

(a) Elimination of initial fast reactions:

Similar to the tests conducted for free chlorine, a 48 hour time period was selected to conduct tests for monochloramine. The initial chlorine concentration added was 1 mg/l. Again all four water types were tested for all chlorine species at pre-determined time intervals. Due to the long-lasting disinfection ability of monochloramine, measurements were taken every second hour for the total period of 48 hours.

The total data set was graphed. Curve fittings were done by applying the least squares method for varying time intervals to again produce the best curve fittings possible.

Similar to free chlorine, these fittings were done firstly by keeping the initial data point constant and changing the final data point e.g. 2 - 48 hours, 2 - 46 hours until a graph for the period 2 - 12 hours was drawn. Secondly the initial point was varied and the final data point kept constant e.g. 2 - 48 hours, 4 - 48 hours until the final graph for the period 36 - 48 hours was drawn.

By analysing these graphs it was clear that during the first four hours, initial fast reactions took place and was therefore inaccurate for inclusion in the standard test procedure. No measurements should therefore be taken during the first four hours.

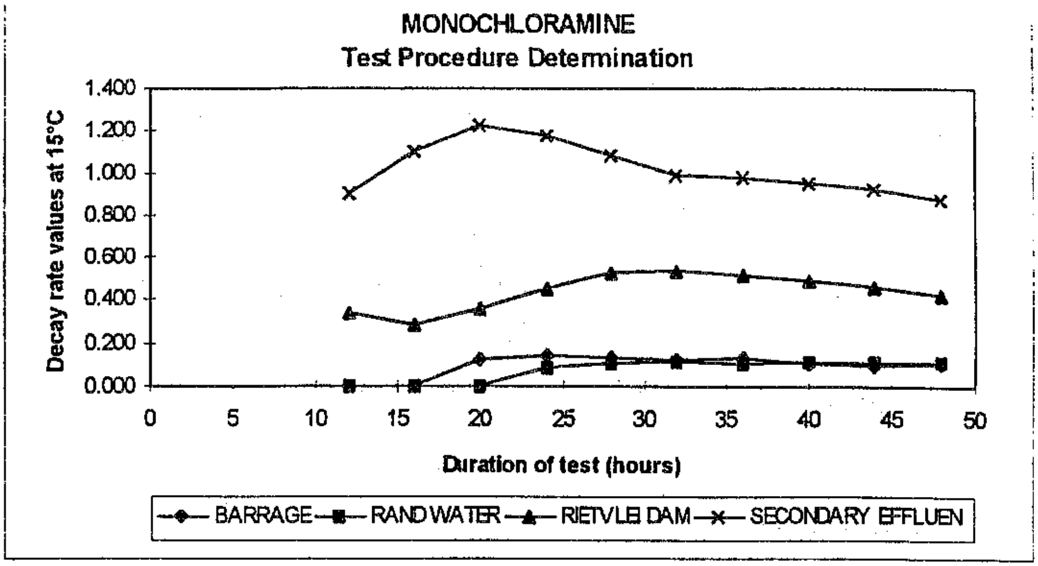
(b) Minimum test duration:

The graphs mentioned above showed that the shortest time period in which to conduct laboratory batch tests was 24 hours, measured every 4 hours. Graph 5.2 represents the effect of the test duration on the first order decay rate constant for monochloramine, shown for the four different raw water types. Each data point represents a decay rate constant obtained from the curve fittings mentioned in section (a). It was evident that after 24 hours the decay rate constant of each different water remained almost the same for each of the different curve fittings with no significant change in the sum of squares.

For two of the raw water sources (Barrage and Vaal Dam), the decay rate constants stabilised if the tests were conducted over periods of 24 hours or larger. For the two other sources, the decay rate constants showed a peak value; for Secondary Effluent at a test duration of 20 hours, and for Rietvlei Dam at 28 hours. As the interest lies in finding the maximum decay rate, a standard test duration of 24 hours was selected for all subsequent chlorine decay tests.

(c) Summary of test procedure:

To determine the chlorine decay rate constant for monochloramine, laboratory experiments should be conducted over a total time period of 24 hours. Measurements should be taken every 4 hours. No measurements should be taken during the first 4 hours of experimental tests.



Graph 5.2. The effect of the test duration on the first order decay rate constant for monochloramine, shown for the four different raw water types

(d) Long-term monochloramine decay tests:

To determine the effect on the chlorine decay rate constant over long time periods, supplementary tests were conducted over a period of 168 hours. The results will be discussed later in sections 5.4.4 and 5.5.4.

5.2.4. Initial dosing concentrations:

(a) Reason for different concentrations:

Three different volumes of the chlorine solution were added to each of the four raw water sources to witness the effect of different concentration levels on the chlorine decay rate and reaction order.

The chlorine decay rate and the reaction order of each sample were calculated for the three concentration levels together. By doing this, it was possible to make conclusions regarding the decay rate and reaction order.

(b) Free chlorine:

The breakpoint of each of the four water types was calculated after a contact period of 20 minutes. Thereafter, three samples of each water were dosed with initial chlorine concentrations of breakpoint + X mg/l, where X denotes 2, 4 and 8 mg/l. This was done to ensure that enough free chlorine would be present to complete the experiments over an 8 hour time period.

(c) Monochloramine:

In the case of monochloramine, three samples of each water were treated with initial monochloramine concentrations of 2, 4 and 8 mg/l. Again this ensured enough monochloramine to be present to complete the experiments over a time period of 24 hours.

5.3. Selection of the most suitable mathematical model:

5.3.1. Mathematical models tested:

Three different mathematical models were tested. Two of them were discussed in Chapter 3, while the third will be described in this section.

The two models already mentioned are:

(a) The first-order, 1 parameter model:

$$C(t) = C_0 e^{-kt} \tag{5.1}$$

(b) The n^{th}-order, 1 parameter model:

$$C(t)=\left[kt(n-1)+\frac{1}{C_0}^{(n-1)}\right]^{\left(-\frac{1}{n-1}\right)} \tag{5.2}$$

(c) The third model is a revised model of the n^{th}-order, 1 parameter model. In order to assure that every graph obtained during data analysis approaches a certain value, an arbitrary value, denoted by X, was introduced in equation (5.2). The revised n^{th}-order, 1 parameter model can therefore be presented as:

$$C(t)=\left[kt(n-1)+\frac{1}{(C_0+X)}^{(n-1)}\right]^{\left(-\frac{1}{n-1}\right)}-X \tag{5.3}$$

where:

$C(t)$ = chlorine concentration at time t (mg/l)

C_0 = initial chlorine concentration (mg/l)

k = nth-order chlorine decay rate constant (1/s)

t = residence time in the pipe

n = order coefficient

X = variable to assure that every graph strives to a certain non-zero value

A general description of this model is that the chlorine decays at a certain rate until a minimum concentration, in this case X, is reached. In the previous model described under (b), the limiting concentration is zero.

5.3.2. Curve fitting procedure:

Each water source was analysed individually. The data for the three different chlorine concentrations (mentioned in section 5.2.4) was analysed for each of the three temperatures used, i.e. 10°C, 15°C and 27°C.

The data were also analysed for each of the three mathematical models. For each model, the decay rate constant, reaction order, X-value and three different initial hypothetical chlorine concentrations (for each of the three temperatures) were calculated. A graph was also drawn for each of the three models, showing three sets of data for the different temperatures.

The least squares method was applied to produce the best curve for calculating the values mentioned above. An example of the curve fitting procedure for free chlorine can be seen in Table 5.1.

Table 5.1. Example of the curve fitting procedure for both free chlorine and monochloramine - shown for free chlorine

CALCULATION SHEET
FREE CHLORINE

GENERAL DATA:

Water source	BARRAGE	
Date of experiment	9-Oct-95	
Water temperature	10	°C
Breakpoint (BP)	1.400	mg/l *(After 20 minutes)*

EXPERIMENTAL DATA:

Time (hour)	Free chlorine BP + 2 mg/l (mg/l)	Free chlorine BP + 4 mg/l (mg/l)	Free chlorine BP + 8 mg/l (mg/l)
0	2.000	4.000	8.000
1	2.570	3.500	4.200
2	2.430	3.500	4.080
3	2.350	3.500	4.010
4	2.280	3.500	3.950
5	2.140	3.450	3.830
6	2.070	3.430	3.760
7	2.000	3.400	3.700
8	1.960	3.380	3.670

CALCULATED RESULTS:

	First order 1 parameter model	n^{th}-order 1 parameter model	Revised n^{th}-order 1 parameter model
X	0.000	0.000	1.690
n	1.000	0.000	0.000
k	0.018	0.061	0.061
C_1	2.411	2.501	2.501
C_2	3.735	3.734	3.734
C_3	4.218	4.176	4.176
Δ_1	-0.411	-0.501	-0.501
Δ_2	0.265	0.266	0.266
Δ_3	3.782	3.824	3.824
Error	0.188	0.128	0.128

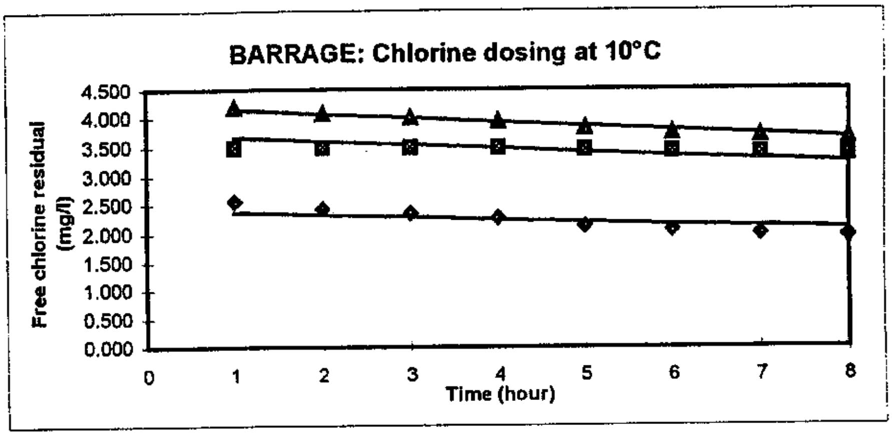
Units:

k - per hour
C_1 - mg/l
C_2 - mg/l
C_3 - mg/l
Δ - difference between the added chlorine and projected chlorine

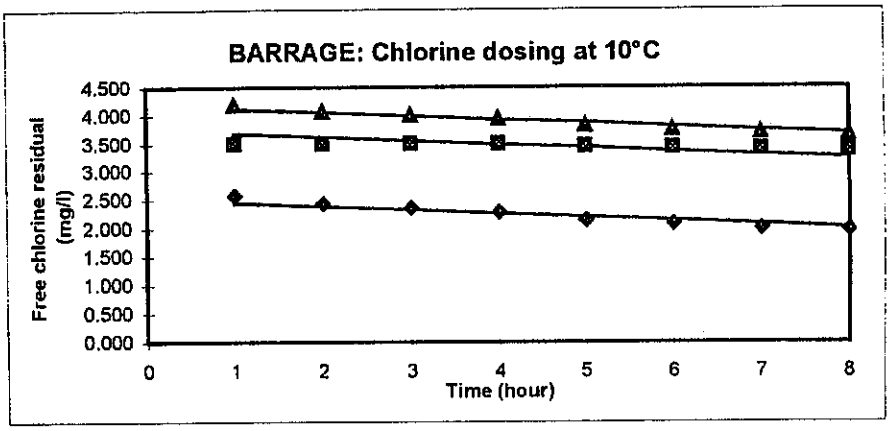
Table 5.1. (Continued) Example of the curve fitting procedure for both free chlorine and monochloramine - shown for free chlorine

GRAPHICAL SHEET
FREE CHLORINE

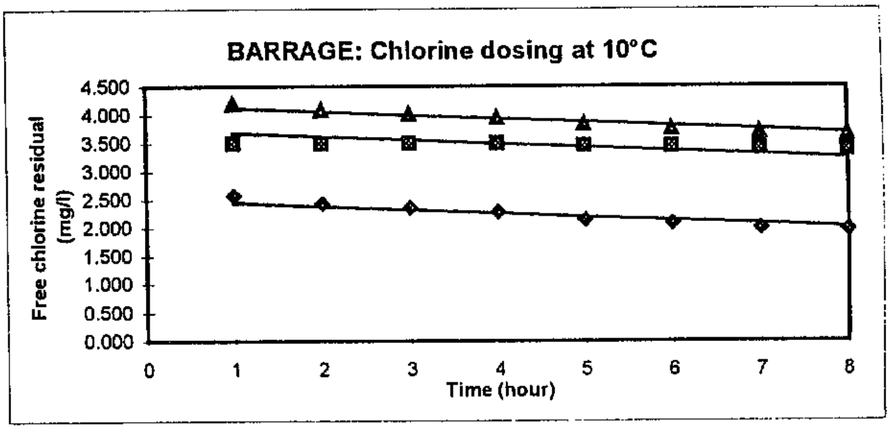
FIRST ORDER, 1 PARAMETER MODEL:



nth-ORDER, 1 PARAMETER MODEL:



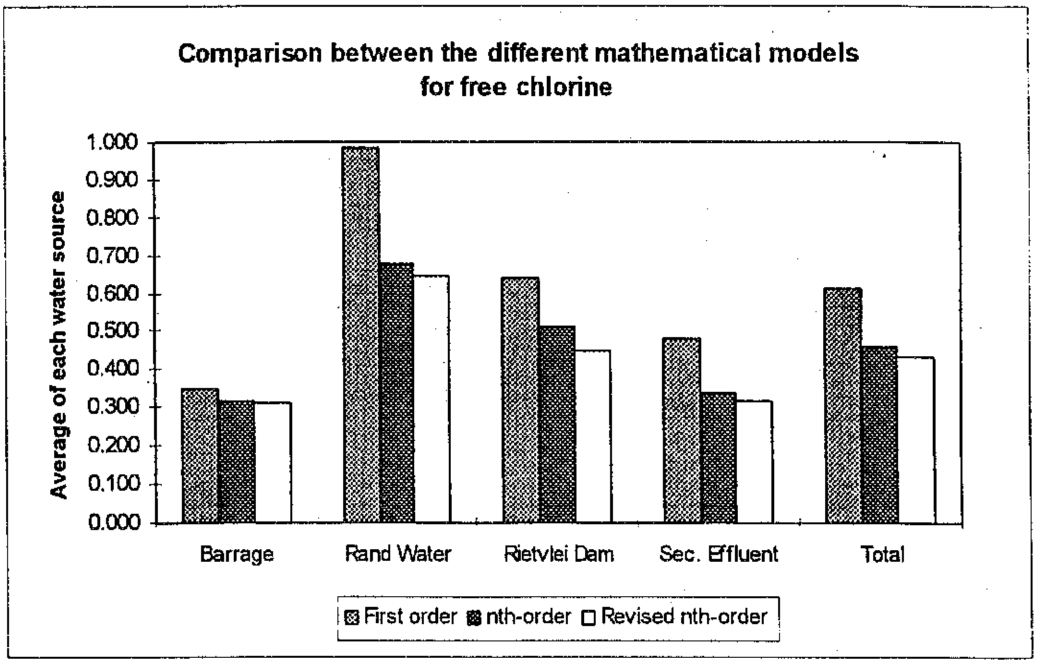
REVISED nth-ORDER, 1 PARAMETER MODEL:



5.3.3. Statistical comparison between mathematical models for free chlorine:

The error values obtained from the least squares method are summarised in Table 5.2. The first step was to compute the standard deviation and sum of squares for each mathematical model and each water source.

As can be seen in Table 5.2, the sum of squares (average of error values) for the first order, 1 parameter model is much higher than those for the nth-order, 1 parameter and revised nth-order, 1 parameter models. The difference between the values of the last two models is much smaller. Graph 5.3 shows the same information (average error values); for each water source as well as for all the sources together.



Graph 5.3. Comparison between the different mathematical models for free chlorine

It is thus clear that the line fittings of the last two models are significantly better than that of the first order, 1 parameter model. It is evident that the difference between the nth-order, 1 parameter model and the revised nth-

order, 1 parameter model is very small. It is clear that the nth-order, 1 parameter model is the best compromise between simplicity and adequate description of the measured data.

Two additional questions were examined:

(a) Are the error values (and thus the quality of fit for different models) significantly different amongst the different water sources?

(b) Are the error values significantly different at different temperatures?

A two-way analysis of variance (ANOVA) (columns = water sources, samples = temperatures) was performed, and the results are shown in Table 5.3. For each cell, there are three values, corresponding to the three dates at which samples were taken. The following conclusions can be drawn from the ANOVA:

- The nth-order, 1 parameter model provides a good fit for all the water sources tested; there is no significant difference between the error values (p = 25.2%).
- The nth-order, 1 parameter model provides a good fit for all the temperatures tested; there is no significant difference between the error values (p = 64.2%).

Table 5.2. Average and standard deviation of the calculated error values

CALCULATED ERROR VALUE SHEET
FREE CHLORINE

FIRST ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.188	0.704	0.993	1.362
	15	0.178	1.448	1.391	1.684
	27	0.960	1.195	0.808	0.797
20-Nov-95	10	0.426	1.561	0.877	0.019
	15	0.276	1.689	0.530	0.031
	27	0.252	1.696	0.134	0.030
25-Jan-96	10	0.499	0.206	0.703	0.128
	15	0.243	0.271	0.259	0.121
	27	0.134	0.102	0.045	0.162
Average of error values		0.351	0.986	0.638	0.482
Standard deviation		0.242	0.630	0.414	0.605

nth-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.128	0.648	0.939	1.010
	15	0.747	0.921	0.800	1.359
	27	0.496	1.159	0.793	0.340
20-Nov-95	10	0.420	0.897	0.870	0.006
	15	0.274	1.057	0.359	0.022
	27	0.221	1.004	0.101	0.079
25-Jan-96	10	0.222	0.150	0.514	0.100
	15	0.211	0.210	0.188	0.119
	27	0.134	0.039	0.041	0.029
Average of error values		0.317	0.676	0.512	0.340
Standard deviation		0.191	0.408	0.332	0.468

REVISED nth-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.128	0.641	0.899	0.958
	15	0.747	0.920	0.800	1.301
	27	0.510	0.909	0.675	0.315
20-Nov-95	10	0.418	0.892	0.715	0.005
	15	0.273	1.080	0.181	0.036
	27	0.221	0.987	0.081	0.017
25-Jan-96	10	0.228	0.162	0.501	0.093
	15	0.178	0.182	0.162	0.101
	27	0.129	0.038	0.040	0.028
Average of error values		0.315	0.646	0.450	0.317
Standard deviation		0.195	0.384	0.317	0.450

Table 5.3. Statistical analysis of the n^{th}-order, 1 parameter model (Error values)

ANALYSIS OF VARIANCE : ERROR VALUES FREE CHLORINE

n^{th}-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.128	0.648	0.939	1.010
20-Nov-95		0.420	0.897	0.870	0.006
25-Jan-96		0.222	0.150	0.514	0.100
9-Oct-95	15	0.747	0.921	0.800	1.359
20-Nov-95		0.274	1.057	0.359	0.022
25-Jan-96		0.211	0.210	0.188	0.119
9-Oct-95	27	0.496	1.159	0.793	0.340
20-Nov-95		0.221	1.004	0.101	0.079
25-Jan-96		0.134	0.039	0.041	0.029

Anova: Two-Factor With Replication

SUMMARY	Barrage	Rand Water	Rietvlei Dam	Sec. Effluent	Total
10					
Count	3.000	3.000	3.000	3.000	12.000
Sum	0.770	1.695	2.323	1.116	5.904
Average	0.257	0.565	0.774	0.372	1.968
Variance	0.022	0.145	0.052	0.307	0.526
15					
Count	3.000	3.000	3.000	3.000	12.000
Sum	1.232	2.188	1.347	1.500	6.267
Average	0.411	0.729	0.449	0.500	2.089
Variance	0.086	0.207	0.100	0.556	0.948
27					
Count	3.000	3.000	3.000	3.000	12.000
Sum	0.851	2.202	0.935	0.448	4.436
Average	0.284	0.734	0.312	0.149	1.479
Variance	0.036	0.368	0.175	0.028	0.607
Total					
Count	9.000	9.000	9.000	9.000	36.000
Sum	2.853	6.085	4.605	3.064	16.607
Average	0.951	2.028	1.535	1.021	5.536
Variance	0.144	0.720	0.326	0.891	2.081

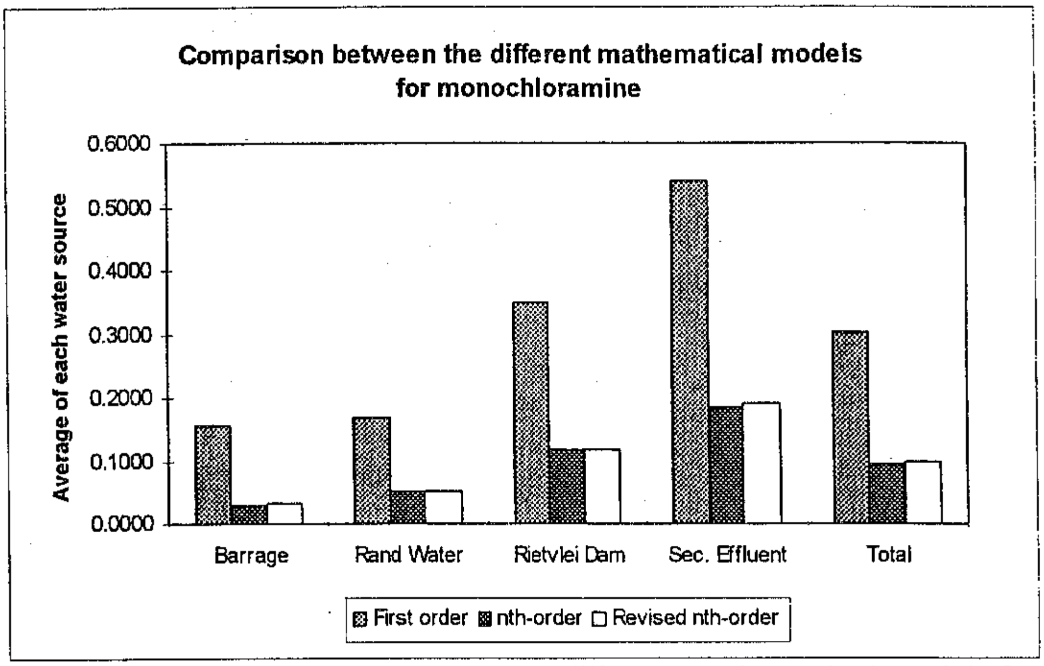
ANOVA

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean sum of squares*	*F-value*	*P-value*	*F-critical*
Sample	0.157	2.000	0.078	0.452	0.642	3.403
Columns	0.757	3.000	0.252	1.455	0.252	3.009
Interaction	0.467	6.000	0.078	0.449	0.838	2.508
Within	4.162	24.000	0.173			
Total	5.543	35.000				

5.3.4. Statistical comparison between mathematical models for monochloramine:

The error values obtained from the least squares method are summarised in Table 5.4. Both the standard deviation and the sum of squares were calculated for each mathematical model and each water source.

As can be seen in Table 5.4, the sum of squares (average of error values) for the first order, 1 parameter model is much higher than those for the nth-order, 1 parameter and revised nth-order, 1 parameter models. The difference between the values of the last two models is much smaller. Graph 5.4 shows the same information (average error values); for each water source as well as for all the sources together.



Graph 5.4. Comparison between the different mathematical models for monochloramine

It is thus clear that the line fittings of the last two models are significantly better than that of the first order, 1 parameter model. It is evident that the difference between the nth-order, 1 parameter model and the revised nth-

order, 1 parameter model is very small. It is clear that the nth-order, 1 parameter model is the best compromise between simplicity and adequate description of the measured data.

Two additional questions were examined:

(a) Are the error values (and thus the quality of fit for different models) significantly different amongst the different water sources?
(b) Are the error values significantly different at different temperatures?

A two-way analysis of variance (ANOVA) (columns = water sources, samples = temperatures) was performed, and the results are shown in Table 5.5. For each cell, there are three values, corresponding to the three dates at which samples were taken. The following conclusions can be drawn from the ANOVA:

- The nth-order, 1 parameter model provides a good fit for all the water sources tested; there is however a difference between the error values (p = 1.31%).
- The nth-order, 1 parameter model provides a good fit for all the temperatures tested; there is no significant difference between the error values (p = 16.29%).

Table 5.4. Average and standard deviation of the calculated error values

CALCULATED ERROR VALUE SHEET
MONOCHLORAMINE

FIRST ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.0335	0.0563	0.1467	0.1249
	15	0.0951	0.1445	0.1216	0.1074
	27	0.0688	0.0949	0.0826	0.1362
20-Nov-95	10	0.1761	0.1035	0.0947	0.5832
	15	0.1635	0.3333	0.1410	0.7881
	27	0.2398	0.1524	1.1198	0.7946
25-Jan-96	10	0.1929	0.1120	0.1032	0.6478
	15	0.1752	0.3556	0.1521	0.8395
	27	0.2484	0.1565	1.1751	0.8219
Average of error values		0.1548	0.1677	0.3485	0.5382
Standard deviation		0.0700	0.0992	0.4278	0.3040

nth-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.0104	0.0151	0.0500	0.0200
	15	0.0066	0.0729	0.0500	0.0060
	27	0.0039	0.0200	0.0195	0.0101
20-Nov-95	10	0.0425	0.0334	0.0235	0.2059
	15	0.0285	0.0752	0.0262	0.2841
	27	0.0440	0.0543	0.3976	0.2998
25-Jan-96	10	0.0464	0.0358	0.0259	0.2275
	15	0.0307	0.0799	0.0289	0.3031
	27	0.0445	0.0581	0.4223	0.3101
Average of error values		0.0286	0.0494	0.1160	0.1852
Standard deviation		0.0164	0.0229	0.1576	0.1268

REVISED nth-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.0103	0.0184	0.0514	0.0148
	15	0.0066	0.0694	0.0586	0.0077
	27	0.0049	0.0296	0.0159	0.0062
20-Nov-95	10	0.0478	0.0289	0.0235	0.2080
	15	0.0281	0.0783	0.0260	0.2880
	27	0.0535	0.0530	0.4007	0.3053
25-Jan-96	10	0.0480	0.0347	0.0258	0.2295
	15	0.0302	0.0815	0.0293	0.3125
	27	0.0520	0.0552	0.4241	0.3285
Average of error values		0.0313	0.0499	0.1173	0.1889
Standard deviation		0.0190	0.0219	0.1584	0.1319

Table 5.5. Statistical analysis of the nth-order, 1 parameter model (Error values)

ANALYSIS OF VARIANCE : ERROR VALUES MONOCHLORAMINE

nth-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.0104	0.0151	0.0500	0.0200
20-Nov-95		0.0425	0.0334	0.0235	0.2059
25-Jan-96		0.0464	0.0358	0.0259	0.2275
9-Oct-95	15	0.0066	0.0729	0.0500	0.0060
20-Nov-95		0.0285	0.0752	0.0262	0.2841
25-Jan-96		0.0307	0.0799	0.0289	0.3031
9-Oct-95	27	0.0039	0.0200	0.0195	0.0101
20-Nov-95		0.0440	0.0543	0.3976	0.2998
25-Jan-96		0.0445	0.0581	0.4223	0.3101

Anova: Two-Factor With Replication

SUMMARY	Barrage	Rand Water	Rietvlei Dam	Sec. Effluent	Total
10					
Count	3.0000	3.0000	3.0000	3.0000	12.0000
Sum	0.0993	0.0843	0.0994	0.4534	0.7364
Average	0.0331	0.0281	0.0331	0.1511	0.2455
Variance	0.0004	0.0001	0.0002	0.0130	0.0137
15					
Count	3.0000	3.0000	3.0000	3.0000	12.0000
Sum	0.0658	0.2280	0.1051	0.5932	0.9921
Average	0.0219	0.0760	0.0350	0.1977	0.3307
Variance	0.0002	0.0000	0.0002	0.0277	0.0280
27					
Count	3.0000	3.0000	3.0000	3.0000	12.0000
Sum	0.0924	0.1324	0.8394	0.6200	1.6842
Average	0.0308	0.0441	0.2798	0.2067	0.5614
Variance	0.0005	0.0004	0.0510	0.0290	0.0810
Total					
Count	9.0000	9.0000	9.0000	9.0000	36.0000
Sum	0.2575	0.4447	1.0439	1.6666	3.4127
Average	0.0858	0.1482	0.3480	0.5555	1.1376
Variance	0.0011	0.0006	0.0514	0.0697	0.1227

ANOVA

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean sum of squares*	*F-value*	*P-value*	*F-critical*
Sample	0.0401	2.0000	0.0200	1.9592	0.1629	3.4028
Columns	0.1355	3.0000	0.0452	4.4171	0.0131	3.0088
Interaction	0.0898	6.0000	0.0150	1.4633	0.2328	2.5082
Within	0.2455	24.0000	0.0102			
Total	0.5108	35.0000				

5.4. Effect of temperature on the reaction order, n:

5.4.1. Objective:

Up to now, the data obtained at each temperature were analysed independently, i.e. the reaction order and decay rate constant were calculated separately for each temperature. One would, however, suspect that the reaction order would not change for a specific water sample, even if tested at different temperatures. The question here, therefore, is:

- Are the reaction orders of the same samples, but measured at different temperatures, statistically significantly different?

If not, the measurements of a single sample, measured at three different temperatures, can be pooled and a single, more reliable reaction order calculated.

5.4.2. Free chlorine:

Due to the different reaction orders calculated for each different data set, it was impossible to compare the different decay rate constants. To overcome this problem a two-way ANOVA was performed (columns = water sources, samples = temperatures). For each cell, there are three values, corresponding to the three dates at which samples were taken. The results are shown in Table 5.6. The following conclusions are drawn:

- The reaction order values are indeed significantly different amongst water sources (p = 2.10%). There is, however no difference between the different temperatures (p = 71.20%), which means that all the data from a specific sample may be pooled to calculate the reaction order.

To further verify these findings, four different two-way ANOVAS were performed (columns = experimental period, sample = temperature), one on each sample individually. The results of the Secondary Effluent are shown in Table 5.7.

- There is no significant difference in reaction order for the same source at different sampling dates (p = 46.80%).
- It is also clear that there is no difference between the reaction orders amongst the different temperatures (p = 35.90%).

The analysis on the other sources showed the same results.

Table 5.6. Statistical analysis of the n^{th}-order, 1 parameter model (Reaction order values)

ANALYSIS OF VARIANCE : REACTION ORDER VALUES
FREE CHLORINE

n^{th}-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.000	1.124	1.123	0.758
20-Nov-95		0.683	0.383	0.899	0.599
25-Jan-96		0.465	0.830	0.520	1.343
9-Oct-95	15	0.000	1.371	1.400	0.787
20-Nov-95		0.814	0.526	1.398	0.658
25-Jan-96		0.566	0.812	0.716	1.077
9-Oct-95	27	0.450	1.075	1.050	0.742
20-Nov-95		0.366	0.476	1.169	0.548
25-Jan-96		1.007	1.269	0.892	0.339

Anova: Two-Factor With Replication

SUMMARY	Barrage	Rand Water	Rietvlei Dam	Sec. Effluent	Total
10					
Count	3.000	3.000	3.000	3.000	12.000
Sum	1.148	2.337	2.542	2.700	8.727
Average	0.383	0.779	0.847	0.900	2.909
Variance	0.122	0.139	0.093	0.154	0.507
15					
Count	3.000	3.000	3.000	3.000	12.000
Sum	1.380	2.709	3.514	2.522	10.125
Average	0.460	0.903	1.171	0.841	3.375
Variance	0.174	0.185	0.155	0.046	0.560
27					
Count	3.000	3.000	3.000	3.000	12.000
Sum	1.823	2.820	3.111	1.629	9.383
Average	0.608	0.940	1.037	0.543	3.128
Variance	0.121	0.171	0.019	0.041	0.352
Total					
Count	9.000	9.000	9.000	9.000	36.000
Sum	4.351	7.866	9.167	6.851	28.235
Average	1.450	2.622	3.056	2.284	9.412
Variance	0.417	0.495	0.268	0.240	1.420

ANOVA

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean sum of squares*	*F-value*	*P-value*	*F-critical*
Sample	0.082	2.000	0.041	0.345	0.712	3.403
Columns	1.386	3.000	0.462	3.904	0.021	3.009
Interaction	0.418	6.000	0.070	0.589	0.736	2.508
Within	2.840	24.000	0.118			
Total	4.725	35.000				

Table 5.7. Statistical analysis of the n^{th}-order, 1 parameter model (Secondary Effluent reaction order values)

ANALYSIS OF VARIANCE : REACTION ORDER VALUES FREE CHLORINE

n^{th}-ORDER, 1 PARAMETER MODEL:

SECONDARY EFFLUENT:

Temperature (°C)	Date 9-Oct-95	20-Nov-95	25-Jan-96
10	0.758	0.599	1.343
15	0.787	0.658	1.077
27	0.742	0.548	0.339

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
10	3.000	2.700	0.900	0.154
15	3.000	2.522	0.841	0.046
27	3.000	1.629	0.543	0.041
9-Oct-95	3.000	2.287	0.762	0.001
20-Nov-95	3.000	1.805	0.602	0.003
25-Jan-96	3.000	2.759	0.920	0.271

ANOVA

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean sum of squares*	*F-value*	*P-value*	*F-critical*
Rows	0.220	2.000	0.110	1.336	0.359	6.944
Columns	0.152	2.000	0.076	0.923	0.468	6.944
Error	0.329	4.000	0.082			
Total	0.700	8.000				

5.4.3. Monochloramine (short-term tests):

The same argument was followed for the analysis of the monochloramine data.

A two-way ANOVA was performed (columns = water sources, samples = temperatures). For each cell, there are three values, corresponding to the three dates at which samples were taken. The results are shown in Table 5.8. The following conclusions are drawn:

- The reaction order values are indeed significantly different amongst water sources (p = 0.60%). There is, however no difference between the different temperatures (p = 25.02%), which means that all the data from a specific sample can be pooled to calculate the reaction order.

To further verify these findings, four different two-way ANOVAS were performed (columns = experimental period, sample = temperature), one on each sample individually. The results of the Secondary Effluent are shown in Table 5.9.

- There is no significant difference in reaction order for the same source at different sampling dates (p = 28.14%).
- It is also clear that there is no difference between the reaction orders for the different temperatures (p = 35.48%).

The analysis on the other sources showed the same results.

Table 5.8. Statistical analysis of the n^{th}-order, 1 parameter model (Reaction order values)

ANALYSIS OF VARIANCE : REACTION ORDER VALUES MONOCHLORAMINE

n^{th}-ORDER, 1 PARAMETER MODEL:

Date	Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
9-Oct-95	10	0.3816	0.1696	0.0548	0.0275
20-Nov-95		0.2122	0.4399	0.2589	0.0591
25-Jan-96		0.2113	0.4427	0.2626	0.0536
9-Oct-95	15	0.0986	0.3211	0.0542	0.0706
20-Nov-95		0.2500	0.0813	0.2442	0.0696
25-Jan-96		0.2484	0.0814	0.2422	0.0705
9-Oct-95	27	0.2120	0.0271	0.2128	0.0130
20-Nov-95		0.2634	0.2459	0.0388	0.1426
25-Jan-96		0.2626	0.2561	0.0380	0.1452

Anova: Two-Factor With Replication

SUMMARY	Barrage	Rand Water	Rietvlei Dam	Sec. Effluent	Total
10					
Count	3.0000	3.0000	3.0000	3.0000	12.0000
Sum	0.8051	1.0522	0.5763	0.1402	2.5738
Average	0.2684	0.3507	0.1921	0.0467	0.8579
Variance	0.0096	0.0246	0.0141	0.0003	0.0487
15					
Count	3.0000	3.0000	3.0000	3.0000	12.0000
Sum	0.5970	0.4838	0.5406	0.2107	1.8321
Average	0.1990	0.1613	0.1802	0.0702	0.6107
Variance	0.0076	0.0192	0.0119	0.0000	0.0386
27					
Count	3.0000	3.0000	3.0000	3.0000	12.0000
Sum	0.7380	0.5291	0.2896	0.3008	1.8575
Average	0.2460	0.1764	0.0965	0.1003	0.6192
Variance	0.0009	0.0167	0.0101	0.0057	0.0335
Total					
Count	9.0000	9.0000	9.0000	9.0000	36.0000
Sum	2.1401	2.0651	1.4065	0.6517	6.2634
Average	0.7134	0.6884	0.4688	0.2172	2.0878
Variance	0.0180	0.0605	0.0362	0.0060	0.1207

ANOVA

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean sum of squares*	*F-value*	*P-value*	*F-critical*
Sample	0.0296	2.0000	0.0148	1.4686	0.2502	3.4028
Columns	0.1600	3.0000	0.0533	5.3011	0.0060	3.0088
Interaction	0.0651	6.0000	0.0108	1.0783	0.4029	2.5082
Within	0.2415	24.0000	0.0101			
Total	0.4961	35.0000				

Table 5.9. Statistical analysis of the n^{th}-order, 1 parameter model (Secondary Effluent reaction order values)

ANALYSIS OF VARIANCE : REACTION ORDER VALUES
MONOCHLORAMINE

n^{th}-ORDER, 1 PARAMETER MODEL:

SECONDARY EFFLUENT:

Temperature (°C)	Date 9-Oct-95	 20-Nov-95	 25-Jan-96
10	0.0275	0.0591	0.0536
15	0.0706	0.0696	0.0705
27	0.0130	0.1426	0.1452

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
10	3.0000	0.1402	0.0467	0.0003
15	3.0000	0.2107	0.0702	0.0000
27	3.0000	0.3008	0.1003	0.0057
9-Oct-95	3.0000	0.1111	0.0370	0.0009
20-Nov-95	3.0000	0.2713	0.0904	0.0021
25-Jan-96	3.0000	0.2693	0.0898	0.0024

ANOVA

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean sum of squares*	*F-value*	*P-value*	*F-critical*
Rows	0.0043	2.0000	0.0022	1.3576	0.3548	6.9443
Columns	0.0056	2.0000	0.0028	1.7701	0.2814	6.9443
Error	0.0064	4.0000	0.0016			
Total	0.0163	8.0000				

5.4.4. Monochloramine (long-term tests):

A two-way ANOVA was performed (columns = water sources, samples = temperatures). The results are shown in Table 5.10. For each cell, the average of two values, corresponding to the two sample dates, was taken. From Table 5.10 it is clear that the reaction order values are not significantly different between the various water sources (p = 53.30%) and temperatures (p = 48.80%).

Table 5.10. Statistical analysis of the n^{th}-order, 1 parameter model (Reaction order values)

ANALYSIS OF VARIANCE : REACTION ORDER VALUES MONOCHLORAMINE

n^{th}-ORDER, 1 PARAMETER MODEL:

Temperature (°C)	Barrage	Rand Water	Rietvlei Dam	Secondary Effluent
10	0.911	0.980	0.929	0.946
15	0.928	0.981	0.951	0.966
27	0.915	0.888	0.975	0.936

Anova: Two-Factor Without Replication

SUMMARY	*Count*	*Sum*	*Average*	*Variance*
10	4.000	3.766	0.942	0.001
15	4.000	3.826	0.957	0.001
27	4.000	3.714	0.929	0.001
Barrage	3.000	2.754	0.918	0.000
Rand Water	3.000	2.849	0.950	0.003
Rietvlei Dam	3.000	2.855	0.952	0.001
Sec. Effluent	3.000	2.848	0.949	0.000

ANOVA

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean sum of squares*	*F-value*	*P-value*	*F-critical*
Rows	0.002	2.000	0.001	0.810	0.488	5.143
Columns	0.002	3.000	0.001	0.806	0.535	4.757
Error	0.006	6.000	0.001			
Total	0.010	11.000				

5.4.5. Re-analysis of the reaction order:

After the data analysis described in sections 5.4.2-5.4.4 was completed, the data was re-analysed. This was done because of the finding that the different temperatures did not have an effect on the reaction order of the different water sources.

The least squares method was applied to all available data for each water source - this included data for the three initial concentrations, as well as for the three different temperatures. By doing this, only one reaction order value was calculated for each water sample, regardless of the different temperatures. An example of the analysis sheet can be seen in Table 5.11.

Table 5.11. Example of the re-analysis curve fitting procedure for both free chlorine and monochloramine - shown for free chlorine

CALCULATION SHEET
FREE CHLORINE

GENERAL DATA:

Water source	VAAL DAM
Date of experiment	9-Oct-95
Breakpoint (BP)	0.700 mg/l

EXPERIMENTAL DATA:

Time (hour)	10°C Free chlorine (mg/l)	15°C Free chlorine (mg/l)	27°C Free chlorine (mg/l)	10°C Free chlorine (mg/l)	15°C Free chlorine (mg/l)	27°C Free chlorine (mg/l)	10°C Free chlorine (mg/l)	15°C Free chlorine (mg/l)	27°C Free chlorine (mg/l)
0	2.600	2.400	2.500	4.600	4.500	4.600	8.500	8.400	8.400
1	1.940	1.100	1.890	4.150	4.300	3.950	7.750	7.800	7.500
2	1.280	0.980	1.470	3.700	3.250	3.300	7.000	6.400	6.600
3	1.050	0.850	1.250	2.940	2.600	2.430	5.750	5.600	5.650
4	1.000	0.750	1.200	2.780	2.110	2.050	5.300	3.950	4.700
5	1.000	0.640	1.190	2.390	2.010	1.910	4.250	3.480	3.630
6	0.810	0.560	1.100	2.300	1.940	1.620	3.480	2.760	2.550
7	0.730	0.470	0.750	2.010	1.860	1.430	3.060	2.500	2.020
8	0.580	0.380	0.550	1.830	1.770	1.260	2.700	2.340	1.890

CALCULATED RESULTS:

n^{th}-order, 1 parameter model

n	1.174	Error	2.930
k_{10}	0.114		
k_{15}	0.145	X	0.000
k_{27}	0.151		
C_1	1.774	Δ_1	0.826
C_2	1.295	Δ_2	1.105
C_3	2.242	Δ_3	0.258
C_4	4.897	Δ_4	-0.297
C_5	4.959	Δ_5	-0.459
C_6	4.681	Δ_6	-0.081
C_7	9.379	Δ_7	-0.879
C_8	9.617	Δ_8	-1.217
C_9	9.859	Δ_9	-1.459

Units:

k - per hour

C_1 - mg/l
C_2 - mg/l
C_3 - mg/l

C_4 - mg/l
C_5 - mg/l
C_6 - mg/l

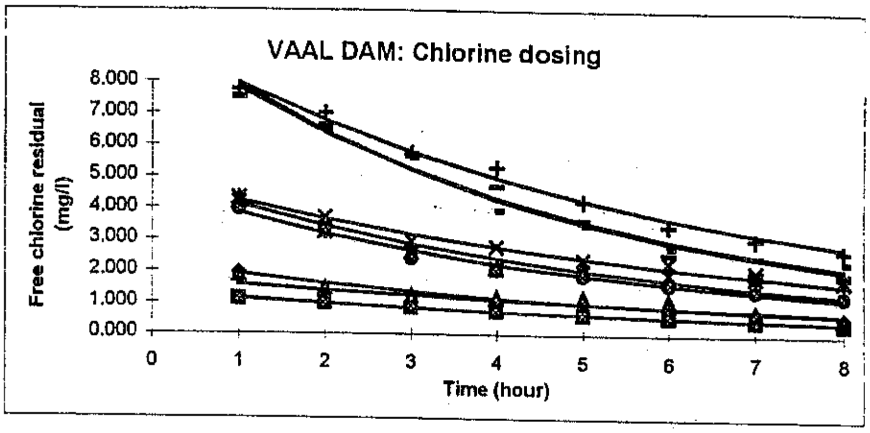
C_7 - mg/l
C_8 - mg/l
C_9 - mg/l

Δ - difference between the added chlorine and projected chlorine

Table 5.11. (Continued) Example of the re-analysis curve fitting procedure for both free chlorine and monochloramine - shown for free chlorine

GRAPHICAL SHEET
FREE CHLORINE

nth-ORDER, 1 PARAMETER MODEL:



(a) Free chlorine:

Table 5.12 represents a summary of all the reaction order values obtained for free chlorine after re-analysis.

Table 5.12. Summary of all reaction order values obtained for free chlorine after re-analysis

Water source	Experimental date		
	9-Oct-95	**20-Nov-95**	**25-Jan-96**
Barrage	0.357	0.602	0.755
Vaal Dam	1.174	0.473	0.916
Rietvlei Dam	1.170	1.213	0.672
Secondary Effluent	0.763	0.659	0.920

(b) Monochloramine (short-term tests):

Table 5.13 represents a summary of all the reaction order values obtained for monochloramine (short-term tests) after re-analysis.

Table 5.13. Summary of all reaction order values obtained for monochloramine (short-term tests) after re-analysis

Water source	Experimental date		
	9-Oct-95	20-Nov-95	25-Jan-96
Barrage	0.205	0.246	0.245
Vaal Dam	0.168	0.240	0.246
Rietvlei Dam	0.102	0.105	0.106
Secondary Effluent	0.022	0.098	0.097

(c) Monochloramine (long-term tests):

Table 5.14 represents a summary of all the reaction order values obtained for monochloramine (long-term tests) after re-analysis.

Table 5.14. Summary of all reaction order values obtained for monochloramine (long-term tests) after re-analysis

Water source	Experimental date		
	9-Oct-95	20-Nov-95	25-Jan-96
Barrage	*	0.917	0.917
Vaal Dam	*	0.951	0.951
Rietvlei Dam	*	0.951	0.951
Secondary Effluent	*	0.949	0.949

5.5. Effect of temperature on the decay rate constant, k:

5.5.1. Free chlorine:

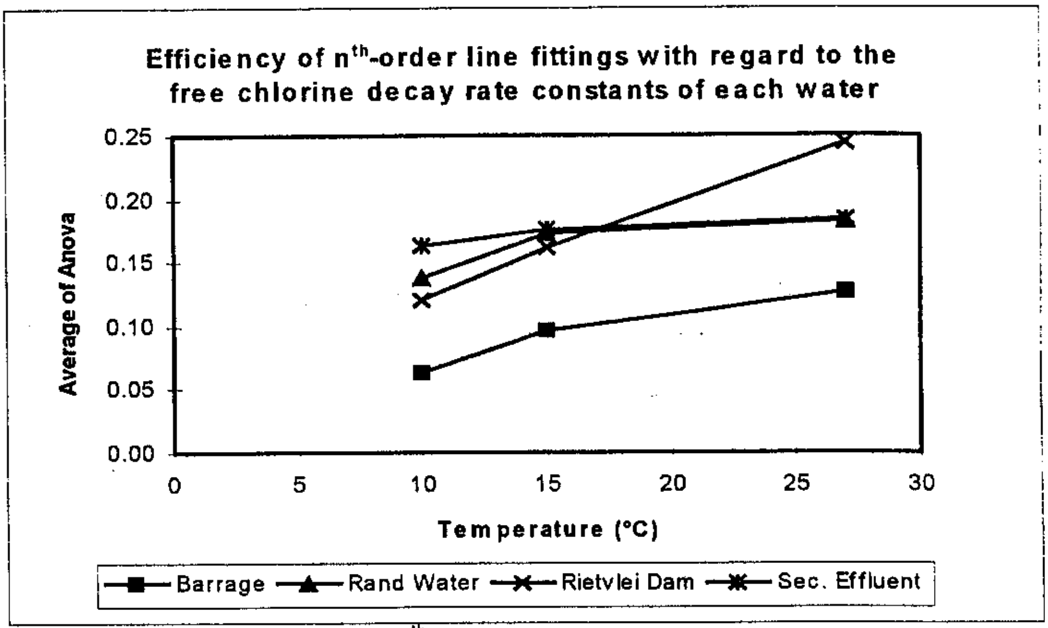
Table 5.15 contains all the decay rate values for each water sample obtained after the re-analysis of the data for free chlorine.

Table 5.15. Decay rate values for each water sample obtained after re-analysis for free chlorine

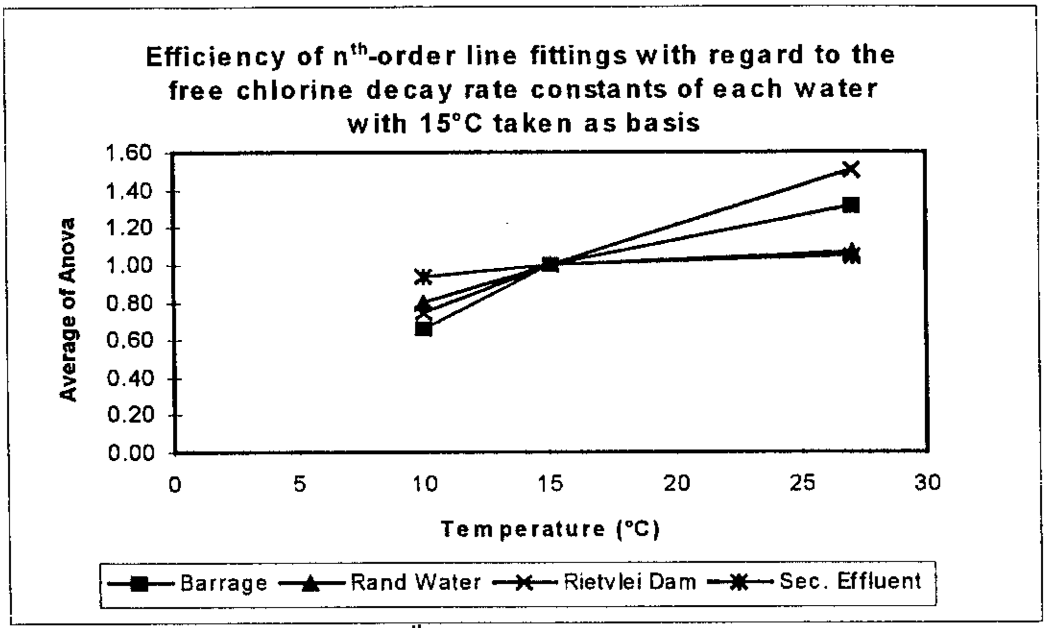
Source	**Date**	**Temperature**		
		10°C	**15°C**	**27°C**
Barrage	9-Oct-95	0.040	0.118	0.158
	20-Nov-95	0.071	0.069	0.073
	25-Jan-96	0.078	0.101	0.147
Vaal Dam	9-Oct-95	0.114	0.145	0.151
	20-Nov-95	0.172	0.257	0.259
	25-Jan-96	0.124	0.114	0.136
Rietvlei Dam	9-Oct-95	0.114	0.144	0.155
	20-Nov-95	0.178	0.252	0.499
	25-Jan-96	0.067	0.091	0.077
Secondary Effluent	9-Oct-95	0.239	0.255	0.273
	20-Nov-95	0.164	0.179	0.180
	25-Jan-96	0.087	0.090	0.097
Average		0.121	0.151	0.184
Deviation in relation to k_{15}		0.801	1.000	1.219

Graph 5.5 represents a summary of the n^{th}-order, 1 parameter model on the efficiency of the n^{th}-order line fittings with regard to the free chlorine decay rate constants of each water.

Graph 5.6 represents the same data with the decay rate value for 15°C taken as basis.



Graph 5.5. Efficiency of n^{th}-order line fittings with regard to the free chlorine decay rate constants of each water



Graph 5.6. Efficiency of n^{th}-order line fittings with regard to the free chlorine decay rate constants of each water with 15°C taken as basis

5.5.2. Monochloramine (short-term tests):

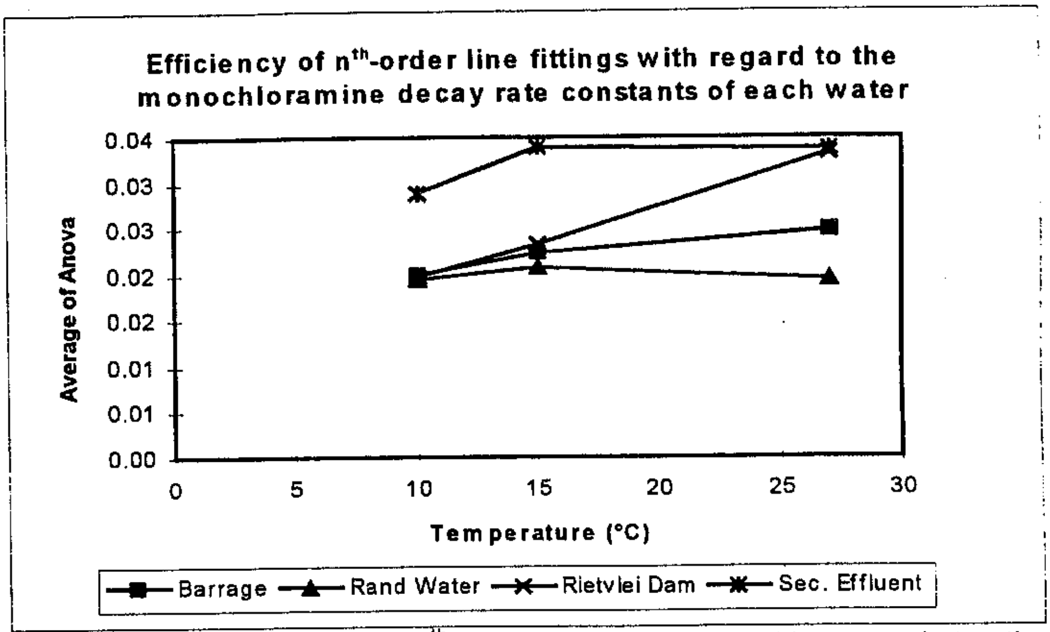
Table 5.16 contains all the decay rate values for each water sample obtained after the re-analysis of the data for monochloramine (short-term tests).

Table 5.16. Decay rate values for each water sample obtained after re-analysis for monochloramine (short-term tests)

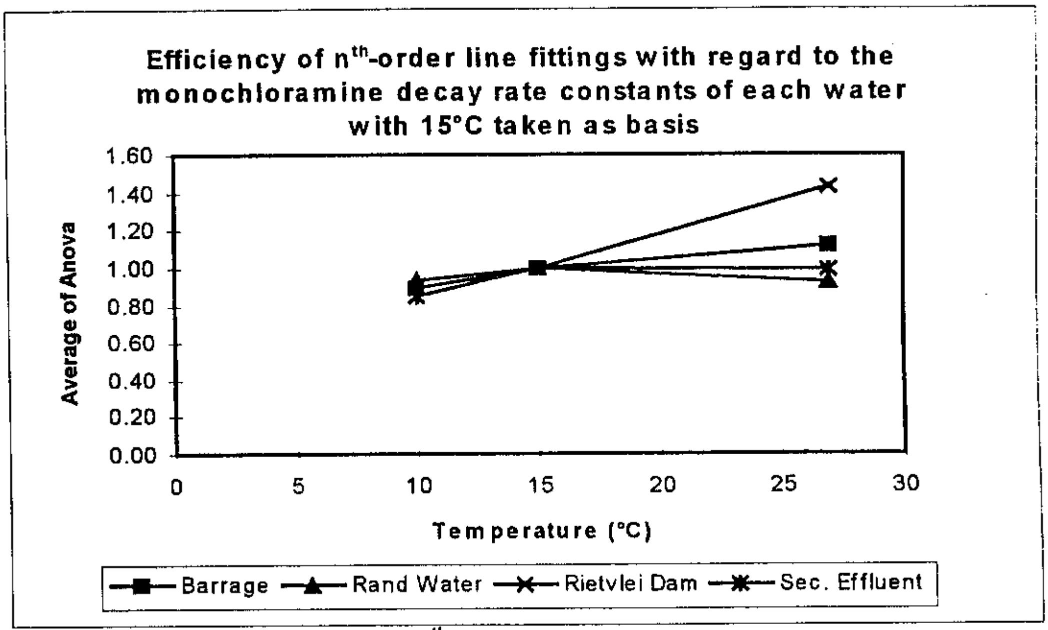
Source	**Date**	**Temperature**		
		10°C	**15°C**	**27°C**
Barrage	9-Oct-95	0.0138	0.0176	0.0177
	20-Nov-95	0.0226	0.0245	0.0283
	25-Jan-96	0.0234	0.0252	0.0288
Vaal Dam	9-Oct-95	0.0097	0.0111	0.0119
	20-Nov-95	0.0240	0.0255	0.0230
	25-Jan-96	0.0247	0.0260	0.0232
Rietvlei Dam	9-Oct-95	0.0147	0.0151	0.0119
	20-Nov-95	0.0217	0.0270	0.0435
	25-Jan-96	0.0226	0.0278	0.0441
Secondary Effluent	9-Oct-95	0.0196	0.0237	0.0198
	20-Nov-95	0.0328	0.0386	0.0402
	25-Jan-96	0.0342	0.0398	0.0410
Average		0.0220	0.0252	0.0278
Deviation in relation to k_{15}		0.8730	1.0000	1.1032

Graph 5.7 represents a summary of the n^{th}-order, 1 parameter model on the efficiency of the n^{th}-order line fittings with regard to the free chlorine decay rate constants of each water.

Graph 5.8 represents the same data with the decay rate value for 15°C taken as basis.



Graph 5.7. Efficiency of n^{th}-order line fittings with regard to the monochloramine decay rate constants of each water



Graph 5.8. Efficiency of n^{th}-order line fittings with regard to the monochloramine decay rate constants of each water with 15°C taken as basis

5.5.3. Monochloramine (long-term tests):

Table 5.17 contains all the decay rate values for each water sample obtained after the re-analysis of the data for monochloramine (long-term tests).

Table 5.17. Decay rate values for each water sample obtained after re-analysis for monochloramine (long-term tests)

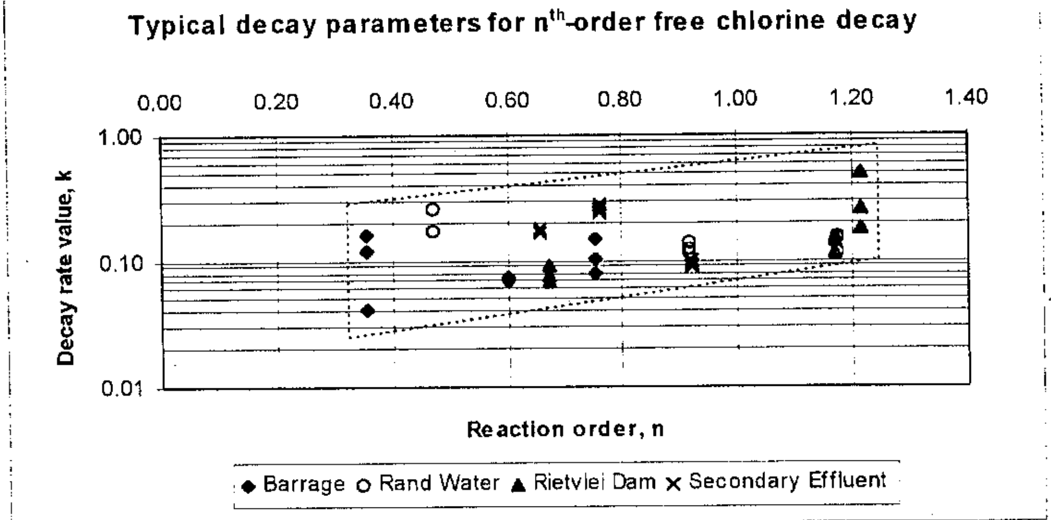
Source	Date	Temperature		
		10°C	15°C	27°C
Barrage	9-Oct-95	*	*	*
	20-Nov-95	0.0131	0.0131	0.0138
	25-Jan-96	0.0132	0.0131	0.0138
Vaal Dam	9-Oct-95	*	*	*
	20-Nov-95	0.0114	0.0118	0.0123
	25-Jan-96	0.0114	0.0118	0.0123
Rietvlei Dam	9-Oct-95	*	*	*
	20-Nov-95	0.0123	0.0124	0.0128
	25-Jan-96	0.0123	0.0125	0.0128
Secondary Effluent	9-Oct-95	*	*	*
	20-Nov-95	0.0126	0.0128	0.0133
	25-Jan-96	0.0126	0.0128	0.0133
Average		0.0124	0.0126	0.0131
Deviation in relation to k_{15}		0.9841	1.0000	1.0397

5.6. Typical ranges of the decay rate constant and the reaction order:

5.6.1. Free chlorine:

Typical decay rate constants obtained during the analysis of the data are summarised in Graph 5.9. It represents the different values for free chlorine laboratory batch tests.

As can be seen in the graph, the typical values obtained for the 1-8 hour time period are k = 0.04 (n = 0.36) to k = 0.50 (n = 1.22).

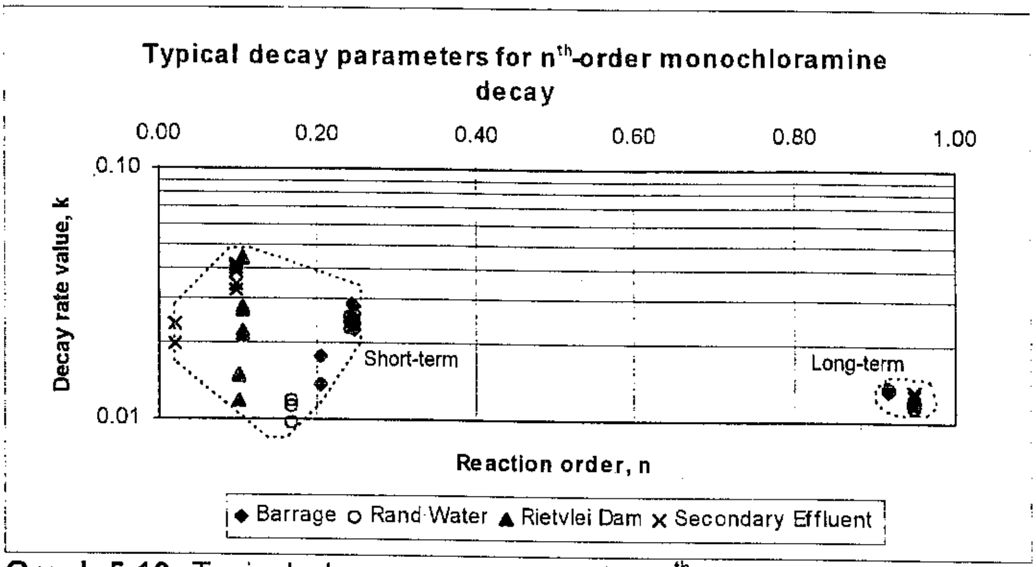


Graph 5.9. Typical decay parameters for n^{th}-order free chlorine decay

5.6.2. Monochloramine (short and long-term tests):

Graph 5.10 represents the typical values for the decay rate constant and reaction order obtained for the 4-24 hour monochloramine experiments. The values range from k = 0.01 (n = 0.02) to k = 0.05 (n = 0.25).

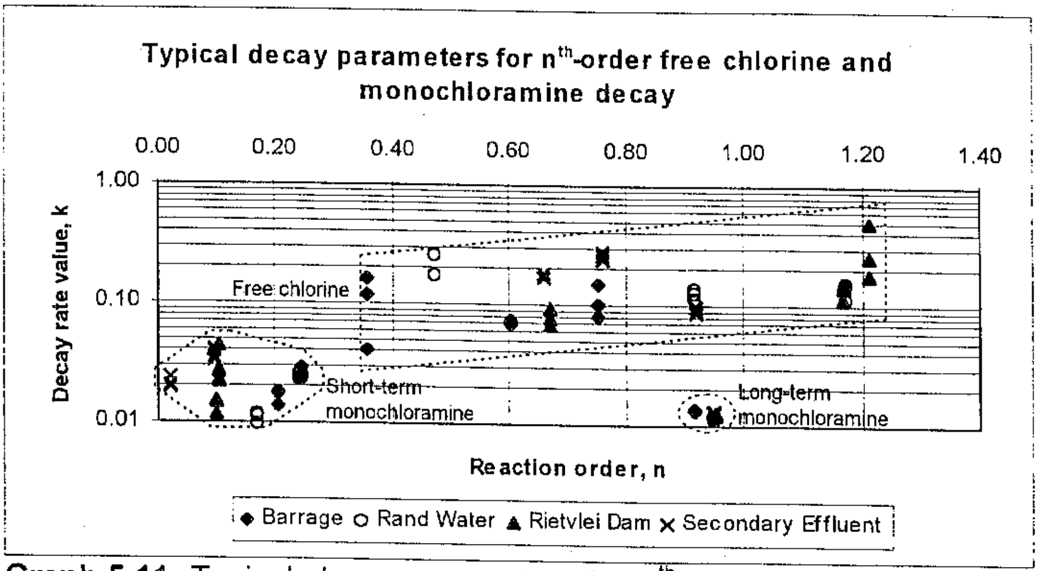
Graph 5.10 also contains the values obtained for the 24-168 hour monochloramine experimental period. The typical values for this time period are concentrated on one point as can be seen in the graph: k = 0.013 (n = 0.95).



Graph 5.10. Typical decay parameters for nth-order monochloramine decay

5.6.3. Combination of values for free chlorine and monochloramine:

By combining Graphs 5.9 and 5.10, Graph 5.11 is obtained.



Graph 5.11. Typical decay parameters for nth-order free chlorine and monochloramine decay

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CHAPTER 6

CHLORINE DECAY BEHAVIOUR IN POTABLE WATER PIPELINES

6.1. Selection of pipeline sections:

After the completion of the laboratory experiments the focus of the study moved to the selected pipeline sections of Rand Water to put into practice the knowledge obtained by the analytical tests. Table 6.1 contains important information regarding the selected pipelines.

Table 6.1. Important pipeline information

	Pipeline number			
	A6	**A8**	**A12**	**A14**
From	Rand Water : Vereeniging pumping station			
To	Rand Water : Zwartkopjes pumping station			
Oxidant	Free chlorine			
Sample point 1				
Description	Tap in pipe			
Distance from Vereeniging	14300 m	14300 m	13800 m	13800 m
Sample point 2				
Description	Tap in pipe			
Distance from Vereeniging	28740 m	28770 m	22980 m	22950 m

The experiments were carried out during summer and winter temperatures to determine the effect of temperature on the chlorine decay. Complete information regarding the pipelines was available, i.e. inside diameter, length, flow rate and temperature.

6.2. Pipeline tests:

6.2.1. Objectives:

Pipeline tests were conducted to compare the bulk water flow decay rate constant with the control water decay rate constant in order to determine the effect of the pipe wall on the chlorine decay.

6.2.2. Analysis procedure:

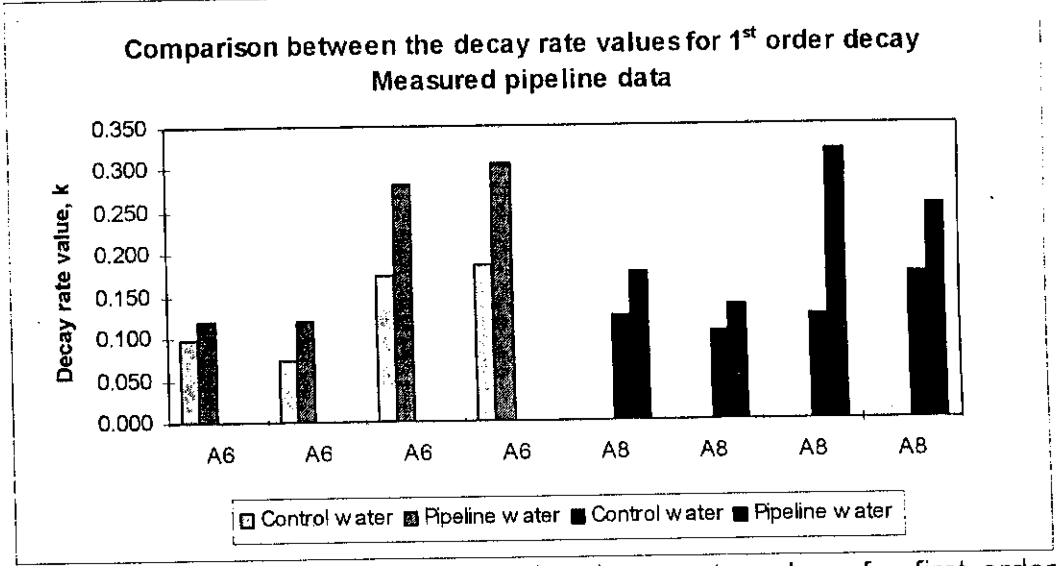
Tests were conducted at three different points on each pipeline selected, i.e. the starting point, an intermediate sampling point and at the end of the pipeline. The three different chlorine species were tested in each case so that the results obtained could be compared.

These tests were compared with a laboratory control test where water was taken from the pipeline at the starting point and stored in an airtight, dark container to determine the influence of the pipe wall on the chlorine decay rate constant. In the case of the control water, measurements were taken in accordance with the standard test procedure developed for free chlorine in Chapter 5.

The calculation sheet provides for the first order case. Firstly the reaction order was set to 1 for both the pipeline experimental data and the control water experimental data. Secondly, the decay rate constant and hypothetical initial chlorine concentration for the control water were calculated by applying the least squares method. Finally, the initial chlorine concentration was kept constant and again the least squares method was applied to calculate the decay rate constant for the pipeline experimental data. This procedure enabled us to compare the decay rate constants for the control water and the pipeline water.

6.2.3. Results:

The difference between the two decay rate values indicated the influence of the pipe wall on the chlorine decay. The difference can be seen graphically on the calculation sheets. The upper line in Table 6.2 represents the chlorine decay in the laboratory control water while the lower line represents the decay as monitored in the pipe itself. In each of the four cases studied, the decay rate for the pipe was higher than for the control water. This indicated a definite influence of the pipe wall on the chlorine decay rate constant.



Graph 6.1. Comparison between the decay rate values for first order decay - measured pipeline data

Table 6.2. shows the calculation sheet for pipeline A6 on 14 November 1995. Graph 6.1. shows the differences between the first order decay

rate constants for the control water and the first order decay rate constants for the bulk water in the pipe.

Table 6.2. Calculation sheet for pipeline A6 on 14 November 1995

CALCULATION SHEET
MEASURED PIPELINE DATA

GENERAL DATA:

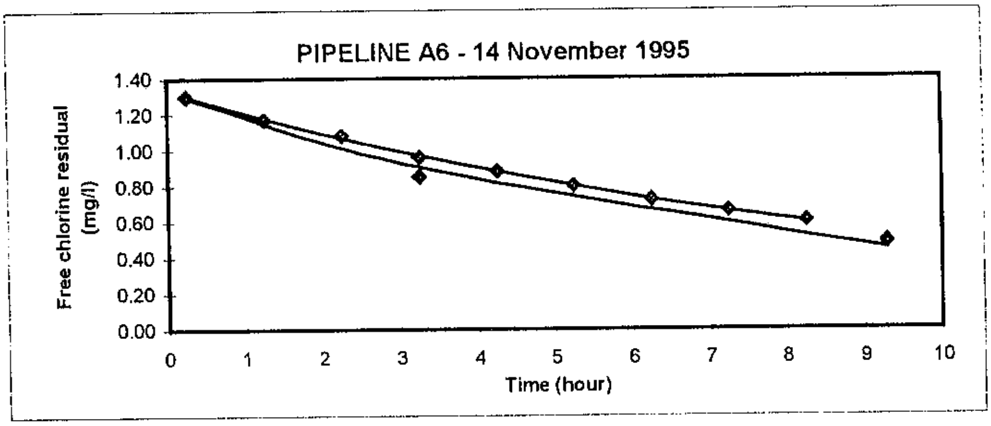
Pipeline number	A6		Sample point 1 to sample point 2	14300	m
Experimental date	14-Nov-95		Sample point 2 to sample point 3	28740	m
Inside pipe diameter	1.120	m	Flow velocity	1.324	m/s
Total pipeline length	43040	m	Flow rate	1.304	m^3/s
Pipe area	0.985	m^2	Temperature	22	°C
			Chlorination to first reading	0.250	h

PIPELINE EXPERIMENTAL DATA AND CALCULATED RESULTS:

Time (hour)	Free chlorine (mg/l)		First order 1 parameter model
0.250	1.300	n	1.000
3.250	0.850	k	0.119
9.280	0.480	C_1	1.329
		Error	0.004

CONTROL WATER EXPERIMENTAL DATA AND CALCULATED RESULTS:

Time (hour)	Free chlorine (mg/l)		First order 1 parameter model
0.250	1.300	n	1.000
1.250	1.170	k	0.097
2.250	1.080	C_1	1.329
3.250	0.960	Error	0.000
4.250	0.880		
5.250	0.800		
6.250	0.720		
7.250	0.660		
8.250	0.600		



6.3. Determination of the wall consumption parameter:

6.3.1. Objective:

The objective in determining the wall consumption parameter was to relate the decay rate of the pipeline to the decay rates of the bulk water and the pipe wall individually.

6.3.2. Mathematical model:

The mathematical model used for calculating the decay rate constants was described in detail in Chapter 3. A brief discussion of the model is presented below. The model can be written as:

$$\theta(c) = -k_b c - \frac{k_f}{R_H}(c - c_w) \tag{3.1}$$

where:

k_b = first-order bulk reaction rate constant (1/s)
c = chlorine concentration in bulk flow (mg/l)
k_f = mass transfer coefficient between bulk flow and pipe wall (m/s)
R_H = hydraulic radius of pipe (m) [= pipe radius/2]
c_w = chlorine concentration at the wall (mg/l)

The mass balance equation for the wall reaction can be seen in equation (3.2).

$$k_f c - k_f c_w = k_w c_w \tag{3.2}$$

where k_w is a wall reaction rate constant.

Solving for c_w yields equation (3.3):

$$c_w = \frac{k_f c}{(k_w + k_f)} \tag{3.3}$$

Substituting equation (3.3) into equation (3.1) results in the following reaction rate expression:

$$\theta(c) = -K.c \tag{3.4}$$

where K is an overall first-order rate constant equal to $k_b + \frac{k_w k_f}{R_H(k_w + k_f)}$.

The mass transfer coefficient, k_f, can be calculated using the dimensionless Sherwood number as follows (See Chapter 3):

$$k_f = \frac{Sh.D}{d}$$

$$Sh = 0.023 Re^{0.83} Sc^{0.333} \quad \text{for } Re \geq 2300 \tag{3.5}$$

$$Sh = 3.65 + \frac{0.0668\left(\frac{d}{L}\right)Re.Sc}{1 + 0.04\left[\left(\frac{d}{L}\right)Re.Sc\right]^{0.67}} \quad \text{for } Re < 2300 \tag{3.6}$$

where:

k_f = mass transfer coefficient
Sh = Sherwood number
Re = Reynolds number [= $qd/(A\nu)$]
Sc = Schmidt number [= ν/D]
d = pipe diameter (m)
L = pipe length (m)

q = flow rate (m^3/s)
A = cross-sectional flow area of the pipe (m^2)
D = molecular diffusivity of chlorine in water (m^2/s)
ν = kinematic viscosity of water (m^2/s)

Equation (3.5) applies to turbulent flow where the mass transfer coefficient is independent of the position along the pipe. For laminar flow, equation (3.6) supplies an average value of the mass transfer coefficient along the length of the pipe.

The procedure by which the wall reaction rate constant was calculated can be summarised as follows. Calculate the:

- Reynolds number
- Schmidt number
- Sherwood number
- Hydraulic radius of the pipe (m)
- Mass transfer coefficient (m/s)
- Wall reaction rate constant (m/h)

Throughout the calculation first order decay was assumed.

6.3.3. **Results:**

The different wall reaction rate constants for the two pipelines are presented in Table 6.3. Table 6.4 contains the overall decay rate constants as well as the bulk water decay rate constants for the two pipelines.

An example of the calculation sheet for the wall reaction rate parameter can be seen in Table 6.5.

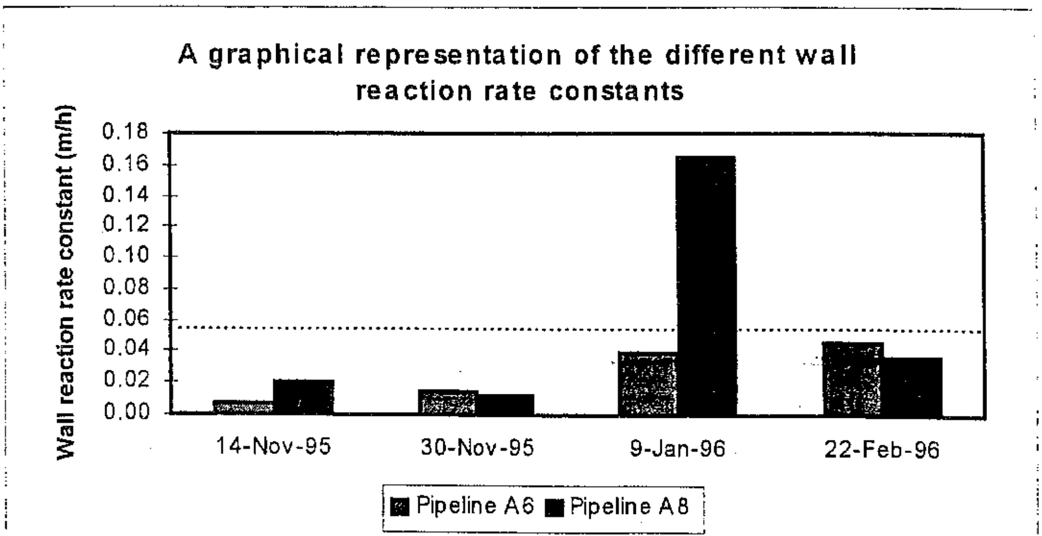
Table 6.3. The different wall reaction rate constants for pipelines A6 and A8

	Wall reaction rate constant (m/h)	
	Pipeline A6	**Pipeline A8**
14 November 1995	0.0065	0.0204
30 November 1995	0.0144	0.0122
9 January 1996	0.0390	0.1653
22 February 1996	0.0457	0.0362

Table 6.4. The overall and bulk water decay rate constants for pipelines A6 and A8

	Overall decay rate constant (1/h)	
	Pipeline A6	**Pipeline A8**
14 November 1995	0.119	0.177
30 November 1995	0.119	0.137
9 January 1996	0.281	0.320
22 February 1996	0.306	0.255
	Bulk water decay rate constant (1/h)	
14 November 1995	0.097	0.125
30 November 1995	0.073	0.105
9 January 1996	0.175	0.125
22 February 1996	0.185	0.175

Graph 6.2 represents a graphical display of the different wall reaction rate constants for pipelines A6 and A8. As can be seen in the graph, the values do not differ very much with the exception of one data point. Due to a larger chlorine decay in pipeline A8 on 9 January 1996 than on the other days, an outlier was created. An upper line can be drawn which includes all wall reaction rate constants as shown below:



Graph 6.2. Representation of the different wall reaction rate constants for pipelines A6 and A8.

Table 6.5. Example of the calculation sheet for the wall reaction rate parameter shown for pipeline A6, 14 November 1995

CALCULATION SHEET

MEASURED PIPELINE DATA

GENERAL DATA:

Pipeline number	A6		Flow velocity	1.324	m/s
Experimental date	14-Nov-95		Flow rate	1.304	m^3/s
Inside pipe diameter	1.120	m	Temperature	22	°C
Total pipeline length	43040	m	Kinematic viscosity of H_2O	1.14E-06	m^2/s
Pipe area	0.985	m^2	Molecular Diffusivity of Cl_2	1.44E-09	m^2/s

DETERMINATION OF THE WALL REACTION RATE CONSTANT:

The determination of the wall reaction rate constant is done in accordance with the first order, 2 parameter mathematical model described in detail in Chapter 3.

Reynolds Number, Re	1.301E+06	
Schmidt Number, Sc	7.917E+02	
Sherwood Number, Sh	2.522E+04	
Hydraulic radius of pipe, R_H	0.280	m
Overall rate constant, K	0.119	1/h
Bulk reaction rate constant, k_b	0.097	1/h
Mass transfer coefficient, k_f	3.242E-05	m/s
Wall reaction rate constant, k_w	0.00650	m/h

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CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. Technical conclusions from the project:

The conclusions drawn from the results presented in this report are:

7.1.1. Conclusions on the measurement of chlorine decay:

(a) All the chemical reactions associated with free chlorine and monochloramine do not occur at the same rate. To eliminate the initial instantaneous reactions from the medium and long term reactions, the first free chlorine reading should only be made after the first hour, and thereafter at hourly intervals. In the case of monochloramine, the first reading should be taken after four hours, and thereafter at four-hourly intervals.

(b) A good estimate of free chlorine decay can be made if the experimental test is continued for a period of eight hours (or longer). For monochloramine, the test period should be at least 24 hours at four-hourly intervals, and at daily intervals thereafter for five days or longer.

(c) In this study, excellent results were obtained if three initial chlorine concentrations were used. For free chlorine, the initial concentrations used were fixed at 2, 4 and 8 mg/l above the 20-minute breakpoint. In the case of monochloramine, the initial concentrations were fixed at 2, 4 and 8 mg/l as Cl_2.

7.1.2. Conclusions on the modelling of chlorine decay:

(a) For both free chlorine and monochloramine, substantially better data fits were obtained if an n^{th}-order decay rate model were used instead of the customary first order decay rate model.

(b) The reaction orders are different for different water sources, and even different for the same water source at different times. For a given sample, however, the reaction orders are independent of temperature.

(c) The rate constants, in all cases, are dependent on temperature. The higher the temperature, the higher the decay rate constants.

(d) The reaction order for free chlorine varied from 0.36 to 1.22, with no apparent underlying pattern. For monochloramine, the reaction order fell into two distinctively different categories. For monochloramine decay up to 24 hours (short-term tests), the reaction order varied from 0.02 to 0.25. For monochloramine decay from 24 hours onwards (long-term tests), the reaction order varied from 0.92 to 0.95.

7.1.3. Conclusions on free chlorine decay in pipelines:

(a) The free chlorine decay rates obtained in pipelines were higher than in parallel bulk decay rate tests, indicating that the pipe walls did contribute significantly to the total decay of free chlorine.

(b) On the assumption that the bulk decay reaction order is equal to one, the mass transfer coefficient between the bulk flow and pipe wall could be calculated. With the exception of a single outlier, the coefficient varied between 0.0065 m/h and 0.0457 m/h.

7.2. Review of project in terms of the initial objectives:

In terms of the original contract with the Water Research Commission, the objectives were to:

(a) Determine typical chlorine decay constants for free and combined chlorine on representative pipeline systems.

(b) Predict chlorine decay in existing and proposed pipelines by using a computerised program.

Upon finishing the project it was clear that significant progress were made in terms of the above objectives. The following specific contributions were made:

(a) A standardised test procedure was developed for the determination of the rate of chlorine decay in simple laboratory batch systems.

(b) The reaction order of chlorine decay was established as an important parameter, and the most suitable mathematical model for the description of chlorine decay was determined.

(c) These methods were applied to a range of widely different quality raw water types and preliminary practical ranges for reaction orders and decay rate constants were established.

(d) The aforementioned batch procedure were combined with actual pipeline tests, and the relative importance of chlorine decay due to the pipe wall was established.

7.3. Recommendations for future study:

(a) The effect of secondary chlorination on different source waters should be studied in order to provide network operators with a practical guide on the possible implementation thereof. In other words, if secondary or tertiary chlorination is practised, will the chlorine decay at the same rate?

(b) More direct methods of estimating pipe wall-related chlorine reaction constants are needed, e.g. conducting a practical test on the pipe wall itself.

(c) The use of strategically placed sensors in the distribution system coupled with remote telemetry might offer a way to perform continuous on-line calibration of network chlorine decay models as conditions change over time.

(d) Water quality models should be enhanced to better accommodate systems where blending of different source waters occurs, where each source water exhibits different bulk reaction kinetics.

(e) The present water quality models for distribution systems, which all assume first order bulk decay, should be updated for n^{th}-order decay to give more realistic results.

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PART 2

THE PREDICTION OF CHLORINE DECAY FROM POTABLE WATER IN PIPELINE SYSTEMS

PRACTICAL GUIDELINE

TABLE OF CONTENTS: PART 2

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THE PREDICTION OF CHLORINE DECAY FROM POTABLE WATER IN PIPELINE SYSTEMS

PRACTICAL GUIDELINE

1. Introduction:

This short guideline is a companion document to Part 1 of this report.

It is intended to summarize the information pertinent to water supply authorities who want to do first-hand measurements of chlorine decay at their own installations. It also provides, by way of practical examples, the mathematical tools required for chlorine decay predictions in pipeline systems.

In this guideline, two chlorine species are considered; free chlorine and monochloramine.

2. Factors influencing chlorine demand:

2.1. Bulk decay rate:

Chlorine decays with time. In the case of free chlorine the reaction takes place quickly and for monochloramine it is slowly. To model the decay of free chlorine as well as monochloramine two important mathematical models need to be considered.

Firstly the first order, one parameter decay model is the simplest of all mathematical models, and is presented in equation (1).

$$C(t) = C_0 e^{-kt} \tag{1}$$

where:

$C(t)$ = Calculated chlorine concentration after time t (mg/l)
C_0 = Initial chlorine concentration (mg/l)
k = Chlorine decay rate (1/h)
t = time (h)

This model is widely accepted in the water industry field.

However, a second model that is also of importance is the nth-order, one parameter decay model. This model is more complicated than the first order, one parameter model but gives better results. It is presented in equation (2).

$$C(t) = \left[kt(n-1) + \frac{1}{C_0}^{(n-1)} \right]^{\left(-\frac{1}{n-1}\right)} \tag{2}$$

where:

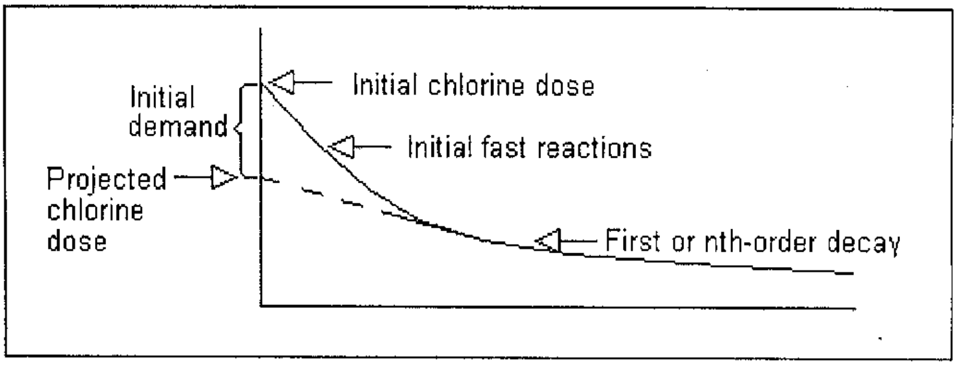
$C(t)$ = Calculated chlorine concentration after time t (mg/l)
C_0 = Initial chlorine concentration (mg/l)
k = Chlorine decay rate (1/h)
t = time (h)

n = reaction order (1>n>1)

2.2. Initial fast reactions:

When experiments are to be conducted, it is necessary to allow sufficient time for initial fast reactions to take place. In the case of free chlorine these fast reactions take place normally in the first hour after initial dosing and thereafter appear to stabilise. To model chlorine decay accurately, no measurements should be taken within the first hour after dosing. In the case of monochloramine this period is extended to the first four hours after initial dosing.

The initial fast reactions can be better illustrated by using a graphical representation.



Graph 1. Graphical representation of the initial fast reactions

2.3. Long-term decay rates:

Free chlorine does not last longer at significant concentrations for longer than a day or two. For this reason, a long-term decay rate over several days is inappropriate.

For monochloramine (which lasts for many days), however, long-term behaviour (longer than a day) is different from the medium-term behaviour (up to 24 hours).

It may therefore be required to model monochloramine long-term decay in two steps - firstly up to 24 hours and secondly from 24 hours onwards.

2.4. Pipe wall effects:

When modelling chlorine decay in pipelines, it is essential that the influence of the pipe wall be taken into account. Not only does chlorine decay occur in the bulk water flow, but also due to the pipe wall. Biofilm on the pipe wall affects the total chlorine decay in any distribution system. The mathematics concerned with this kind of decay is presented in equation (3).

$$\theta(c) = -k_b c - \frac{k_f}{R_H}(c - c_w) \tag{3}$$

where:

k_b = first-order bulk reaction rate constant (1/s)

c = chlorine concentration in bulk flow (mg/l)

k_f = mass transfer coefficient between bulk flow and pipe wall (m/s)

R_H = hydraulic radius of pipe (m) [= pipe radius/2]

c_w = chlorine concentration at the wall (mg/l)

By solving for k_w it is possible to calculate the wall consumption parameter. Equations (4-7) contains the necessary information to calculate k_w.

$$K = k_b + \frac{k_w k_f}{R_H(k_w + k_f)} \tag{4}$$

$$k_f = \frac{Sh.D}{d} \tag{5}$$

$$Sh = 0.023\,Re^{0.83}Sc^{0.333} \quad \text{for } Re \geq 2300 \tag{6}$$

$$Sh = 3.65 + \frac{0.0668\left(\frac{d}{L}\right)Re.\,Sc}{1 + 0.04\left[\left(\frac{d}{L}\right)Re.\,Sc\right]^{0.67}} \quad \text{for } Re < 2300 \tag{7}$$

where:

k_f = mass transfer coefficient

Sh = Sherwood number

Re = Reynolds number [= qd/(Aν)]

Sc = Schmidt number [= ν/D]

d = pipe diameter (m)

L = pipe length (m)

q = flow rate (m^3/s)

A = cross-sectional flow area of the pipe (m^2)

D = molecular diffusivity of chlorine in water (m^2/s)

ν = kinematic viscosity of water (m^2/s)

3. Measurement of chlorine demand parameters:

3.1. Bulk decay rate:

Standardised test procedures for free chlorine and monochloramine can be used to ensure that experiments are carried out in exactly the same manner throughout experimental periods.

For free chlorine, experiments should be conducted for a total period of eight hours. Measurements should be taken on the hour. No measurements must however be taken during the first hour after initial dosing to allow for the stabilisation of initial fast reactions.

In the case of monochloramine medium-term tests, experiments should be conducted for a total period of 24 hours. Measurements should be taken every four hours. No measurements must however be taken during the first four hours after initial dosing to again allow for the stabilisation of initial fast reactions.

3.2. Mathematical curve fitting:

When all the data is obtained, it must be graphed to determine the projected initial chlorine concentration, C_0, the chlorine decay rate, k, and in the case of the n^{th}-order decay rate model, also the reaction order, n.

By using the least-squares curve fitting method, the best fit through the obtained data points can be calculated. The least-squares method can be described as follows:

(a) Calculate the projected chlorine concentration, C_0, and the chlorine decay rate, k, by using either the first order, one parameter or the n^{th}-order, one parameter model.

(b) Calculate the difference between the projected and measured chlorine concentrations and take the square of the answer.

(c) Calculate the sum of all these squared values calculated over the desired experimental period.

(d) Solve for the best answer, i.e. change the initial values for C_0 and k until the sum value is at a minimum.

3.3. Initial fast reactions:

The nature of the initial fast reactions can be determined by subtracting the projected initial chlorine concentration calculated by using the least-squares method from the initial chlorine dosing.

3.4. Pipeline decay rate:

In order to determine the chlorine decay in pipelines, it is necessary that certain parameters be obtained before the modelling of the pipeline can take place. These parameters include the pipe length, withdrawal point distances in relation to the total pipe length, inside pipe diameter and the flow velocity in the pipe.

When all this data is available the flow rate as well as the time it takes for the water to reach a certain point can be calculated.

Conducting experiments at pre-determined withdrawal points in the pipeline, and plotting this data points versus time, the chlorine decay pattern for that pipeline can be determined.

Again by using the least-squares method, the initial chlorine concentration, C_0, the chlorine decay rate, k, and in the case of the n^{th}-order decay rate model, also the reaction order, n, can be calculated for the specific pipeline.

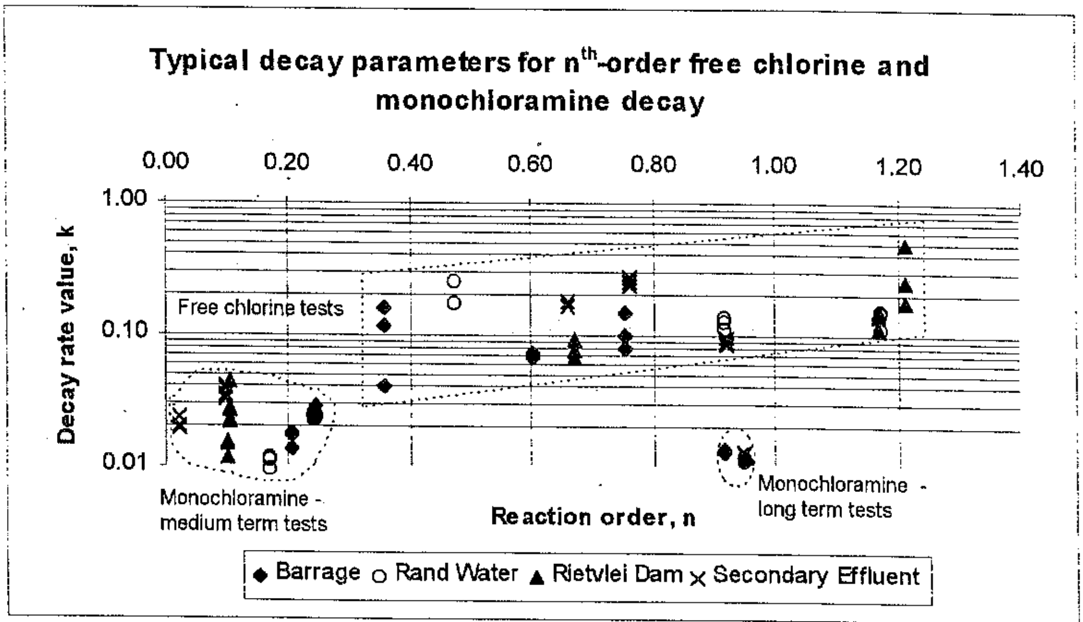
To determine the influence of the pipe wall on chlorine decay it is necessary to conduct a parallel batch test in conjunction with the pipeline test. The difference between the parameter values for the pipeline and batch tests, indicates the effect of the pipe wall.

4. Typical chlorine demand parameters from this study:

4.1. Bulk decay - Rate constants and reaction orders:

Four different water sources were examined throughout the experimental period, i.e. Vaal Dam, Barrage, Rietvlei Dam and Secondary Effluent from the Vereeniging wastewater treatment plant. The first round of experimental tests were used to calculate the standard test procedures discussed earlier. Thereafter three rounds of experiments were conducted namely in October 1995, November 1995 and January 1996.

Graph 2 contains the typical values obtained for the chlorine decay rate constant, k, and for the reaction order, n.

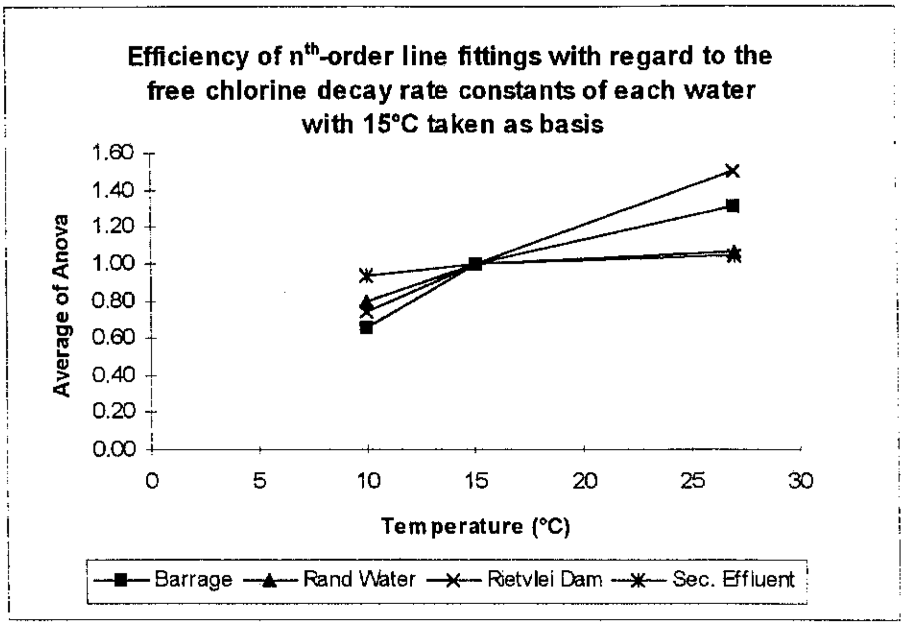


Graph 2. Typical decay parameters for n^{th}-order free chlorine and monochloramine decay

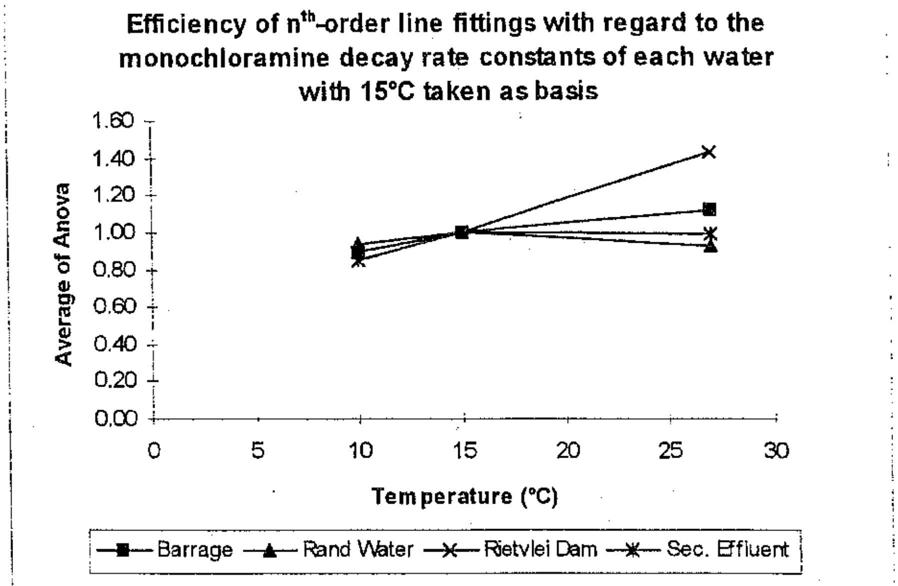
For free chlorine the parameter values range from k = 0.04 (n = 0.36) to k = 0.50 (n = 1.22). For monochloramine medium-term tests the values range from k = 0.01 (n = 0.02) to k = 0.05 (n = 0.25). The values for the long-term monochloramine tests are concentrated on one point as can be seen in the graph: k = 0.013 (n = 0.95).

By studying the graph it is clear that the reaction orders seldomly were equal to one. It is therefore recommended that the n^{th}-order, one parameter is used to obtain better results.

4.2. Temperature effects:



Graph 3. Efficiency of free chlorine line fittings - 15°C as basis



Graph 4. Efficiency of monochlorine line fittings - 15°C as basis

4.3. Pipe wall consumption parameter:

Pipeline tests were conducted on pipelines A6 and A8 of Rand Water. These pipelines start at Vereeniging pumping station and stretches to Zwartkopjes pumping station. Three rounds of experiments were conducted during October 1995, November 1995 and January 1996.

Table 1 contains the typical values obtained for the pipe wall consumption parameter. In the case of the pipeline tests, first order decay kinetics were assumed because of the lack of availability of degrees of freedom when the n^{th}-order model was used. The reaction order is therefore equal to one throughout the pipeline tests.

Table 1. The different wall reaction rate constants for pipelines A6 and A8

	Wall reaction rate constant (m/h)	
	Pipeline A6	**Pipeline A8**
14 November 1995	0.0065	0.0204
30 November 1995	0.0144	0.0122
9 January 1996	0.0390	0.1653
22 February 1996	0.0457	0.0362

As can be seen in the table, all the values are very close to one another with the exception of one high value. This value may however be an outlier.

5. Calculation examples:

5.1. Example 1 - Mathematical curve fitting:

The calculation sheet for pipeline A6, 14 November 1995 is shown directly after Example 3. The sheet consists of three sections. Firstly a general data section which contains information regarding the date and pipeline. Secondly the measured experimental pipeline data and calculated results are presented. Lastly the measured experimental control water data and calculated results complete the calculation sheet.

Since a calculation sheet for pipeline tests is shown, only the first order, one parameter model is presented. However, when only laboratory batch tests are to be conducted, the nth-order, one parameter model should be used instead.

By dividing the distance by the flow velocity, the time it takes for the water to reach the different withdrawal points can be calculated. Initial values for the decay rate constant, k, and the initial chlorine concentration, C_1, must be chosen.

By using equation (1) for first order kinetics, a hypothetical chlorine concentration can be calculated (not shown). By calculating the difference between the measured and calculated concentrations and taking the square thereof, the sum of all these square values can be obtained. By using computer programs and solving for the minimum value of the sum, projected values for the initial chlorine concentration, C_1, and decay rate constant, k, are calculated.

If the nth-order, one parameter decay model were used instead, an additional value for the reaction order, n, would also have been calculated.

5.2. Example 2 - Prediction of bulk chlorine decay:

If the chlorine concentration at time t = 16 hours must be calculated, it can be done for both the first order as well as the nth-order decay models. Only the first order results will be shown by using the values on the calculation sheet in section 5.1.

$t = 16$ hours

$C_1 = 1.329$ mg/l

$k = 0.097$ per hour

$$C(t) = C_1 e^{-kt}$$
$$\therefore C(16) = 1.329 e^{-(0.097 * 16)}$$
$$\therefore C(16) = 0.282 \text{ mg/l}$$

5.3. Example 3 - Prediction of chlorine decay in a pipeline:

By using the mathematics shown in section 2.4 the wall consumption parameter can be calculated. The calculation sheet shown below shows how this parameter can be calculated.

CALCULATION SHEET
MEASURED PIPELINE DATA

GENERAL DATA:

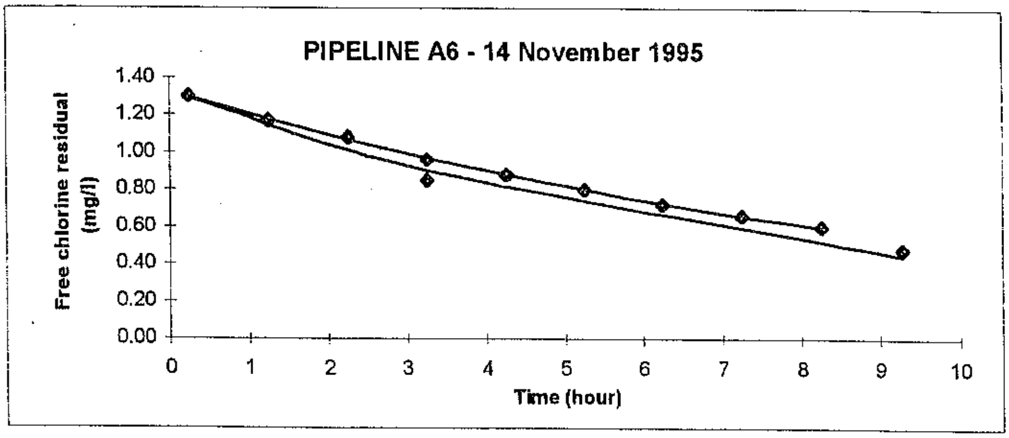
Pipeline number	A6		Sample point 1 to sample point 2	14300	m
Experimental date	14-Nov-95		Sample point 2 to sample point 3	28740	m
Inside pipe diameter	1.120	m	Flow velocity	1.324	m/s
Total pipeline length	43040	m	Flow rate	1.304	m³/s
Pipe area	0.985	m²	Temperature	22	°C
			Chlorination to first reading	0.250	h

PIPELINE EXPERIMENTAL DATA AND CALCULATED RESULTS:

Time (hour)	Free chlorine (mg/l)	First order 1 parameter model	
0.250	1.300	n	1.000
3.250	0.850	k	0.119
9.280	0.480	C_1	1.329
		Error	0.004

CONTROL WATER EXPERIMENTAL DATA AND CALCULATED RESULTS:

Time (hour)	Free chlorine (mg/l)	First order 1 parameter model	
0.250	1.300	n	1.000
1.250	1.170	k	0.097
2.250	1.080	C_1	1.329
3.250	0.960	Error	0.000
4.250	0.880		
5.250	0.800		
6.250	0.720		
7.250	0.660		
8.250	0.600		



CALCULATION SHEET
MEASURED PIPELINE DATA

GENERAL DATA:

Pipeline number	A6		Flow velocity	1.324	m/s
Experimental date	14-Nov-95		Flow rate	1.304	m^3/s
Inside pipe diameter	1.120	m	Temperature	22	°C
Total pipeline length	43040	m	Kinematic viscosity of H_2O	1.14E-06	m^2/s
Pipe area	0.985	m^2	Molecular Diffusivity of Cl_2	1.44E-09	m^2/s

DETERMINATION OF THE WALL REACTION RATE CONSTANT:

The determination of the wall reaction rate constant is done in accordance with the first order, 2 parameter mathematical model described in section 1.4.
A detailed derivation of the applicable mathematics can be seen in the report, Chapter 3.

Reynolds Number, Re	1.301E+06	
Schmidt Number, Sc	7.917E+02	
Sherwood Number, Sh	2.522E+04	
Hydraulic radius of pipe, R_H	0.280	m
Overall rate constant, K	0.119	1/h
Bulk reaction rate constant, k_b	0.097	1/h
Mass transfer coefficient, k_f	3.242E-05	m/s
Wall reaction rate constant, k_w	0.00650	m/h

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