THE USE OF CHLORAMINATION AND SODIUM SILICATE TO INHIBIT CORROSION IN MILD STEEL PIPES

JHB Joubert • JC Geldenhuys • JJ Celliers

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Water Research Commission

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Final report prepared for the Water Research Commission

by

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EXECUTIVE SUMMARY

Distribution and reticulation systems for potable water represent a large proportion of the capital invested by water suppliers. These installations are prone to damage by corrosive water that leads to inconvenience to the consumer when water supply is disrupted and financial losses in the repair and maintenance thereof. In many incidents, unaccounted water losses can be related directly to leaking pipelines as a result of corrosion.

Corrosion in long pipelines and in reticulation systems can be managed by controlling the calcium carbonate precipitation potential (CCPP) of the purified water by adjustment of the pH and alkalinity levels. This method is not consistently successful as the adjustment of the desired parameters is not always practically possible due to shortcomings in plant design or a lack of technical knowledge.

There is evidence that monochloramine and sodium silicates can effectively be administered to inhibit corrosion. However, it is seldom utilized for that purpose in the production and distribution of potable water.

The use of monochloramine could serve a two-fold purpose. It is primarily used to preserve microbiological quality of water in a distribution system and as a bacteriostat to prevent biofouling. Secondly, it could be used as corrosion inhibitor. The advantage of chloramination is that trihalomethanes, additional to those formed during the primary disinfection with breakpoint chlorination are not formed, nor are total organic halogens or mutagenicity levels increased.

Sodium silicate is easy to administer and do not pose a health threat since it is non-toxic in the concentrations normally used. It is inexpensive, tasteless, colourless and odourless in water and has no detrimental environmental effects.

The objectives of the research program were as follows:

1. To determine the extent by which corrosion in steel pipes can be inhibited or reduced by the use of monochloramine or sodium silicates;
2. To determine whether these two chemicals can be used in combination with any type of coagulant;
3. To determine the optimal dosages requirements of the chemicals and the conditions necessary for its effective use.

Two distinct experiments were undertaken, namely a trial based on weight loss of mild steel coupons exposed to water treated in nine different ways and a second trial with mild steel electrodes exposed to water treated in the same way in which the corrosion rates were measured with electro-chemical techniques.

The aim of the two experiments was to measure both short term and long-term effects on the corrosivity of mild steel with different treatments.

The results show clearly that the initial corrosion rates are very high and do not reflect the method of treatment. From this it can be concluded that the long-term performances of a corrosion inhibitor should not be judged on observations made during the first few weeks of exposure of coupons. The time before equilibrium was reached for the experiments described in this document was seven weeks.

In the weight-loss experiments, lower corrosion rates were measured with the addition of monochloramine, even when it was dosed in combination with sodium silicate. Lower corrosion rates were measured with incremental higher dosages.

The addition of only sodium silicate had no effect on the measured corrosion rate as compared with the control sample without any additives. Although the analysis of the corrosion products indicated the presence of silicate, it can be concluded that it had no effect on the corrosion rate. However, there is overwhelming evidence in the literature that support the claim that sodium silicate is an effective corrosion-inhibitor. It is possible that the duration of the experiments was not long enough to observe its effect since sodium silicate is only effective when the tertiary corrosion products, which provide better protection against corrosion, are formed.

The rapid scanning technique demonstrated completely different results. The I_{corr} values with the monochloramine treatments demonstrated higher corrosion rates compared with the control and the treatments with only sodium silicate. An analysis of the data, where the I_{corr} values are plotted in relation with the E_{corr} values, demonstrates that there is a narrow region of E_{corr} values where corrosion is limited. At a surface potential below or above these values, increased corrosion rates are measured. The results clearly show that, at higher monochloramine concentrations, higher corrosion rates are measured. At lower dosages, corrosion is also stimulated.

It appears then that there is a narrow margin within which the monochloramine concentration should be maintained to protect the mild steel pipelines. It also appears that it is in the same level of 1-2 mg/ℓ as required for bacteriostatic activity.

This has a significant practical implication since monochloramine can be used to passivate the surface of corroding metal, provided that concentrations are controlled within the required limits.

It is recommended that in order to optimise the use of monochloramine, field tests should be conducted at several points in a distribution network in order to find a correlation between the surface potential of the pipeline, the monochloramine concentration in the bulk of the water, the bacteriological quality of the water and the corrosion rate.

RECOMMENDATIONS FOR FUTURE RESEARCH

It is recommended that:-

- a study into the mechanism of corrosion inhibition by monochloramine and silicate be conducted
- an investigation into the application of monochloramine and silicate as corrosion inhibitors in water with chemical composition typical to the soft coastal waters compared to harder inland waters be conducted.
- an investigation into the use of monochloramine and silicate as corrosion inhibitors for metals other than mild steel, such as copper tubing, be conducted.

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The steering committee for this project consisted of the following people:

Mr J Bhagwan	Water Research Commission (Chairman)
Ms LA Boyd	Water and Waste Directorate
Mr JJ van der Walt	Magalies Water Board
Mr JHB Joubert	Rand Water
Mr J Opperman	Bloem Water
Ms MJF Krüger	Midvaal Water Company
Mr JC Geldenhuys	Rand Water
Mr M Pryor	Umgeni Water
Ms CM Smit	Committee Secretary

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DEFINITIONS AND SYMBOLS

a(M)	=	activity of species
β	=	Tafel constant
C_B	=	Concentration of reacting species in bulk solution
η_a	=	overvoltage
E^0	=	the standard e.m.f. of a cell when all the species are at unit activity
F	=	Faraday's constant
i	=	rate of oxidation or reduction in terms of current density
i_0	=	exchange current density
K	=	thermodynamic equilibrium constant
r_{oxid}	=	equilibrium oxidation rate
r_{red}	=	equilibrium reduction rate
ν	=	number of electrons transferred in the reduction step
x	=	thickness of the diffusion layer
z	=	number of electrons transferred

CHAPTER 1

1. BACKGROUND TO AND OBJECTIVES OF PROJECT

1.1 Introduction

Distribution and reticulation systems for potable water represent a large proportion of the capital invested by water suppliers. These installations are prone to damage by corrosive water that leads to inconvenience to the consumer when water supply is disrupted and financial losses in the repair and maintenance thereof. In many incidents, the unaccounted water losses can be related directly to leaking pipelines as a result of corrosion.

Corrosion in long pipelines and in reticulation systems can be managed by controlling the calcium carbonate precipitation potential (CCPP) of the purified water by adjustment of the pH and alkalinity levels. This method is not consistently successful as the adjustment of the desired parameters is not always practically, possible due to shortcomings in plant design or a lack of technical knowledge.

There is evidence that monochloramine and sodium silicates can effectively be administered to inhibit corrosion. However, it is seldom utilized for that purpose in the production and distribution of potable water.

The use of monochloramine could serve a two-fold purpose. It is primarily used to preserve microbiological quality of water in a distribution system and as a bacteriostat to prevent biofouling. Secondly, it could be used as corrosion inhibitor. The advantage of chloramination is that trihalomethanes, additional to those formed during the primary disinfection with breakpoint chlorination are not formed, nor are total organic halogens or mutagenicity levels increased.

Sodium silicate is easy to administer and do not pose a health threat since it is non-toxic in the concentrations normally used (Lahodny-Šarc and Kaštelan, 1981). It is inexpensive, tasteless, colourless and odourless in water and has no detrimental environmental effects.

1.2 Objectives

The objectives of the research program were as follows:

1. To determine the extent by which corrosion in steel pipes can be inhibited or reduced by the use of monochloramine or sodium silicates;
2. To determine whether these two chemicals can be used in combination with any type of coagulant;
3. To determine the optimal dosages requirements of the chemicals and the conditions necessary for its effective use.

1.3 Work programme

Two distinct sets of experiments were undertaken, namely a trial based on weight loss of mild steel coupons exposed to water treated in nine different ways and a second trial with mild steel electrodes exposed to the same nine treatment methods in which the corrosion rates were measured with electro-chemical techniques.

The aim of the two experiments was to measure both short term and long-term effects on the corrosivity of mild steel exposed to water that were treated in different ways.

1.4 Outline of document

In the first part of the document, corrosion mechanisms and models involved in the corrosion of mild steel are described. An overview of the chemistry of monochloramine and sodium silicate is given with the emphasis on their properties that may explain their behavior as corrosion inhibitors.

The experimental procedures are then described, followed by a discussion of the results.

In the final chapter, concluding statements are made in terms of the objectives and recommendations for future research work are made.

CHAPTER 2

2. THEORETICAL BACKGROUND OF THE CORROSION AND PASSIVATION OF MILD STEEL

2.1 Introduction

Corrosion is generally defined as the deterioration of a material because of a reaction with its environment (Singley, Deberry, Beaudet, Kidwell, Markey and Malish, 1985; Benefield, Judkins and Weand, 1982). Corrosion of metals, such as mild steel, is a result of an oxidation-reduction chemical reaction. A metal is passive when lower than expected corrosion rates are measured in an environment where it should corrode or at increased anodic potentials (*more noble potentials*) (The Johns Hopkins University Corrosion and Electrochemistry Research Laboratory, 1989; Fontana, 1987).

When mild steel is corroded, iron hydroxides and oxides are typically formed in a cycle of events (Benefield *et al.*, 1982). The specific environmental conditions determine the preferred pathways by which the end products are formed. If one understands the factors that favour one pathway above another, it would be possible to control the rate of corrosion by following the correct strategy.

In the first part of this chapter, an overview is given with respect to the general chemical reactions that may occur during the corrosion of mild steel and the conditions that favour or retard that specific reaction. These reactions include reduction-oxidation reactions, precipitation of slightly soluble reaction products, adsorption on surfaces and gas-liquid reactions. Since all these reactions take place simultaneously and the overall process can be very complicated, an attempt is made to present it in a very simple manner so that the major effects of the corrosion inhibitors can be demonstrated.

In the remainder of the chapter, a brief overview is given with respect to the some general corrosion models to explain some of the research observations.

2.2 Reduction-oxidation and precipitation reactions

Corrosion of mild steel takes place as a result of a net flow of current between a cathode and an anode connected to an external circuit to allow transport of current. When corroding, numerous microscopically cathodic and anodic sites occur on the surface of a mild steel sample. As a result of irregularities such as impurities in the solid or uneven surfaces some areas are nobler than other areas, which are randomly distributed. The metal itself acts as a conductor to allow the flow of electrons between the anodic and cathodic sites. However, to maintain electro-neutrality, ions are transported in the aqueous medium and thereby complete the circuit. The electrical conductivity of metals is much higher than the conductivity of the aqueous medium or electrolyte. Consequently, the electrical conductivity of the medium often plays a significant role in the determination of the corrosion rate.

It is necessary to distinguish between the anodic and cathodic reactions. Some of the anodic reactions and its dependence on environmental conditions are discussed below, followed by a similar discussion of the cathodic reactions.

2.3 Anodic Reactions

At the primary level, solid iron, $Fe_{(s)}$ is oxidised in an aqueous environment at the anode with the formation of dissolved ferrous iron, Fe^{2+}, according to the following half reaction:

$$Fe_{(s)} \rightarrow Fe^{2+} + 2e^{-}$$

When the magnitude of the forward and backward reaction rates of this half reaction is equal, it is in equilibrium and the corrosion rate is zero. This equilibrium state is accurately defined by thermodynamic principles. This condition is satisfied for pure iron when the surface potential equals –0.44 V under standard conditions. It implies that any condition that alters the surface potential may affect the corrosion rate. Based on Le Châvelier's principal, the continuous removal of either the electrons or the dissolved ferrous ions from solution or both will force the reaction to the right and therefore enhance the corrosion rate. The removal of the electrons is dependent on a suitable electron acceptor at the cathode. These reactions will be discussed under cathodic reactions.

Of importance in this section, is the rate of removal of ferrous ions from the solution at the anodic sites. The ferrous ions can be removed either through precipitation reactions or through oxidation to ferric iron. These reactions are typically referred to as secondary and tertiary level anodic reactions (AWWA Research Foundation, 1985; Loewenthal, Wiechers and Marais, 1986; Brits, Geldenhuys, Kok, and Baxter, 1998). Ferrous ions also escape as a result of diffusion from the metal surface through the boundary liquid/metal film into the bulk of the fluid.

Description of the secondary level reactions:

Two precipitation reactions are typically observed whereby ferrous hydroxide, $Fe(OH)_{2(s)}$, or siderite, $FeCO_{3(s)}$, is formed. The two reactions are as follows:

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_{2(s)}\downarrow + 2H^{+}$$

and

$$Fe^{2+} + CO_3^{2+} \rightarrow FeCO_{3(s)}\downarrow$$

The solubility products of the two reactions are $1.8x10^{-15}$ and $2x10^{-11}$ respectively and the precipitation takes place readily. No electron transfer takes place in these two reactions and the absence or presence of an electron acceptor (oxidant) is immaterial (Loewenthal *et al.*, 1986). This is therefore an example where the reaction is forced to the right as a result of the continuous removal of ferrous ions. It is important to note that there is no charge neutralisation in the former reaction. This means that an equivalent quantity of charged protons are formed for each ferrous iron that precipitates. Thus there is always a net balance of positively charged ions. In order to maintain electroneutrality, anions must migrate to the anodic site. This reaction is therefore enhanced in the presence of an electrolyte. In the absence of an electrolyte, no transfer of anions can take place and the corrosion ceases. This is the reason why hardly any corrosion is observed in water that contains little or no dissolved salts.

The former reaction is dependent on the pH of the solution while the latter reaction is dependent on both the pH and carbonate content of the solution. Both reactions are therefore important in a well-buffered medium.

When an electron acceptor such as dissolved oxygen or chlorine is present, the dissolved or precipitated ferrous ion will be oxidised to ferric ions. The Fe^{2+}/Fe^{3+}-half reaction is as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

Dissolved oxygen reacts as follows in an acidic solution:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

or as follows in a neutral solution:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Examining the reactions in an acidic environment, the sum of the half reactions yields the following:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

In a neutral environment, ferrous ion is oxidised as follows:

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$$

Fe^{3+} can be precipitated as $Fe(OH)_{3\,(s)}$:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3\,(s)}\downarrow + 3H^+$$

The precipitation of ferric hydroxide is rapid compared with the oxidation of ferrous to ferric ions (Loewenthal *et al.*, 1986). The oxidation reaction is therefore the rate-limiting step. The oxidation of ferrous ions to ferric ions is a function of factors such as pH and the partial pressure of dissolved oxygen (Stumm and Morgan, 1981)

The oxidation rate can be expressed as follows:

$$-\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}] \times 10^{2pH} \times pO_2$$
$$= \frac{d[Fe^{3+}]}{dt}$$

This function demonstrates that the oxidation rate is particularly pH sensitive. A pH difference of 1 relates to a 100-fold change in the reaction rate.

No electron transfer takes place in the precipitation reaction. Once ferric ions are formed, the absence or presence of an electron acceptor is immaterial. This reaction is, however, dependent on pH.

The overall oxidation and precipitation reaction in either acidic or neutral environments is:

$4Fe^{2+} + O_2 + 10H_2O \rightarrow Fe(OH)_{3\,(s)}\downarrow + 2H^+$

Similarly, dissolved chlorine or monochloramine can act as electron acceptors, too.

For free residual chlorine, the half reaction is as follows:

$2HOCl + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$

Chlorine dissolves in water to yield hydrochlorous acid and hydrochloric acid:

$Cl_2 + H_2O \rightarrow HOCl + HCl$

When combined with the Fe^{2+}/Fe^{3+}-half reaction the overall reaction with dissolved chlorine is as follows:

$2Fe^{2+} + HOCl + H^+ \rightarrow 2Fe^{3+} + Cl^- + H_2O$

With precipitation, the reaction is as follows:

$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_{3\,(s)}\downarrow + 5H^+ + Cl^-$

When monochloramine is dosed, the oxidising half reaction is as follows (White, 1972):

$2NH_2Cl + 2H^+ + e^- \rightarrow Cl_2 + 2NH_3$

and it reacts with ferrous ion in the following manner:

$2Fe^{2+} + 2NH_2Cl + 2H^+ \rightarrow 2Fe^{3+} + Cl_2 + 2NH_3$

After oxidation, ferric hydroxide precipitates to yield the following overall reaction:

$$2Fe^{2+} + 2NH_2Cl + 6H_2O \rightarrow 2Fe(OH)_{3\,(s)} \downarrow + 4H^{+} + Cl_2 + 2NH_3$$

It can be demonstrated that the overall charge in all these reactions is positive. In order to maintain electro-neutrality, migration of anions to the anodic site is important. It can therefore be assumed that the reactions will be accelerated at higher electrolyte concentrations.

The secondary level anodic reactions are followed by tertiary level anodic reactions.

Once the secondary level anodic metastable precipitates, $Fe(OH)_{3\,(s)}$, $Fe(OH)_{2\,(s)}$ and $FeCO_{3\,(s)}$ have been formed, they may be transformed to the stable oxides hematite, γFe_2O_3, and magnetite, Fe_3O_4. The anodic reaction pathways are neutral to alkaline and acidic media as illustrated in Figures 2.1 and 2.2.

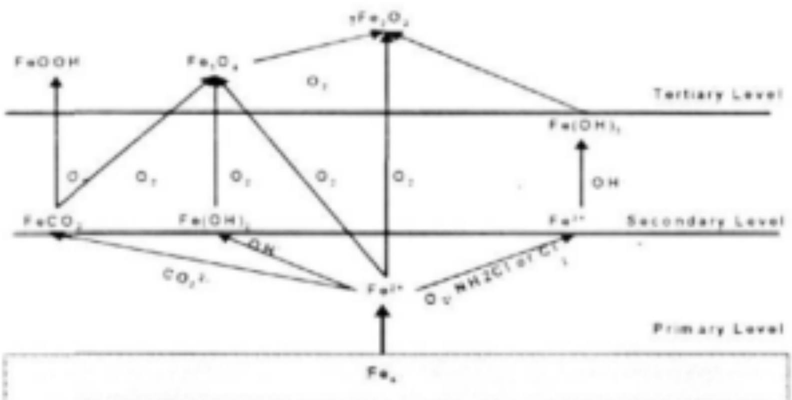


Figure 2.1 Anodic reaction pathways for iron in contact with neutral to alkaline water (Adapted from Loewenthal *et al.*, 1986)

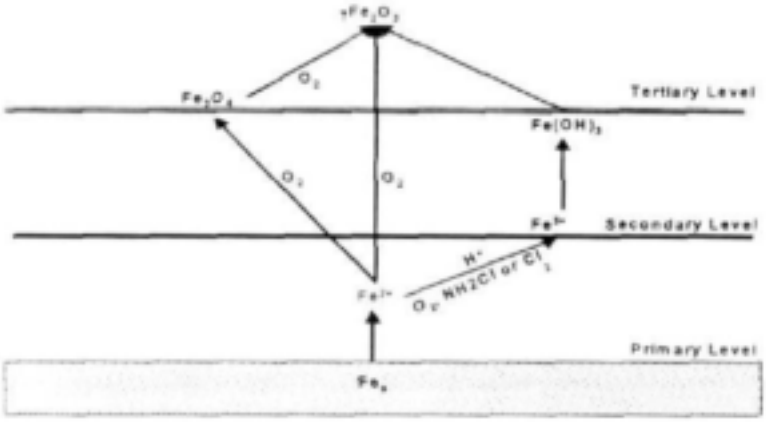


Figure 2.2 Anodic reaction pathways of iron under acidic conditions (Adapted from Loewenthal *et al.*, 1986)

The following reactions will most likely take place.

(i) <u>$Fe(OH)_{3\,(s)}$ transformation to γFe_2O_3:</u>

$$Fe(OH)_{3\,(s)} \rightarrow \gamma Fe_2O_{3\,(s)} + 3H_2O$$

(ii) <u>$Fe(OH)_{2\,(s)}$ transformation to γFe_2O_3</u>

$$6Fe(OH)_{2\,(s)} + O_2 \rightarrow 2Fe_3O_{4\,(s)} + 6H_2O$$

The magnetite is then transformed to hematite by further oxidation:

$$4Fe_3O_{4\,(s)} + O_2 \rightarrow 6\gamma Fe_2O_{3\,(s)}$$

The overall reaction for the transformation of the metastable ferrous hydroxide precipitate to hematite is as follows:

$$4Fe(OH)_{2\,(s)} + O_2 \rightarrow 2\gamma Fe_2O_{3\,(s)} + 4H_2O$$

(iii) <u>$FeCO_{3\,(s)}$ transformation to FeOOH or to γFe_2O_3 via Fe_3O_4</u>

Goethite is formed as follows:

$$4FeCO_{3\,(s)} + O_2 + 2\,H_2O \rightarrow 4FeOOH_{(s)} + 4CO_2\uparrow$$

Alternatively, magnetite is formed and then transformed into hematite:

$$6FeCO_{3\,(s)} + O_2 \rightarrow 2Fe_3O_{4\,(s)} + 6CO_{2\,(g)}\uparrow$$

and upon further oxidation, hematite is formed as follows:

$$4Fe_3O_{4\,(s)} + O_2 \rightarrow 6\gamma Fe_2O_{3\,(s)}$$

The overall reaction is then:

$$4FeCO_{3\,(s)} + O_2 \rightarrow 2\gamma Fe_2O_{3\,(s)} + 4CO_{2\,(g)}\uparrow$$

The evolution of gaseous carbon dioxide during this reaction causes a localised decrease in pH.

(iv) Fe^{2+} transformed to $Fe_3O_{4\,(s)}$ or $\gamma Fe_2O_{3\,(s)}$

Magnetite or hematite may be formed directly as a result of the oxidation of ferrous ion by dissolved oxygen. For the formation of magnetite,

$$6Fe^{2+} + O_2 + 6H_2O \rightarrow 2Fe_3O_{4\,(s)} + 12H^+$$

For the formation of hematite,

$$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2\gamma Fe_2O_{3\,(s)} + 8H^+$$

In all but the reactions of group (iv) the compounds are electro-neutral and therefore not dependent on the presence of electrolytes. The opposite applies to the direct oxidation of ferrous irons to either magnetite or hematite. In the latter case, these reactions will proceed faster at increased levels of conductivity. Conditions that favour the availability of dissolved oxygen are important.

At oxygen levels higher than 1 mg/ℓ, the stable end products are goethite, FeOOH, or hematite, γFe_2O_3. At extremely low dissolved oxygen concentrations siderite, $FeCO_3$, and/or magnetite, Fe_3O_4, are typical reaction end products.

2.4 Cathodic reactions

As the electrons are generated at the anodic site and transferred to the cathodic site, electron acceptors consume it. The electron acceptors that might play a role in this investigation are dissolved oxygen, chlorine and monochloramine.

The typical half reactions are already listed above, but are repeated for convenience sake.

Reactions of dissolved oxygen

in an acidic solution,

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

in a neutral solution,

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

For free residual chlorine, the half reaction is as follows:

$$2HOCl + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$$

Chlorine dissolves in water to form hypochlorous acid and hydrochloric acid:

$$Cl_2 + H_2O \rightarrow HOCl + [H^+ + Cl^-]$$

Hypochlorous acid dissociates as follows:

$$HOCl \leftrightarrow H^+ + OCl^-$$

Inserting the last two reactions in the chlorine half reaction yields

$$2HOCl + 2e^- \rightarrow OCl^- + Cl^- + H_2O$$

The modified Pourbaix diagram in Figure 2.3 illustrates the different corrosion products that can be expected under metastable equilibrium conditions but will also be a function of the prevailing kinetic conditions.

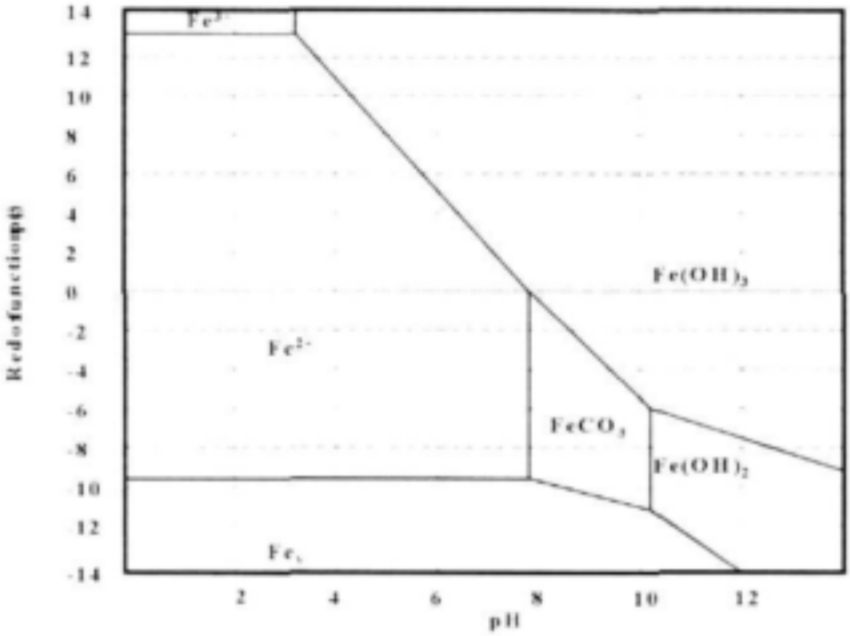


Figure 2.3 pe-pH diagram for metastable equilibrium of the iron-carbonate-water system. $Fe_T = 10^{-5}$ moles/ℓ, $C_T = 10^{-3}$ moles/ℓ and temperature 25 °C. (Redrawn from Loewenthal *et al.*, 1986).

When monochloramine is dosed, the oxidation half reaction is as follows:

$$2NH_2Cl + 2H^+ + 2e^- \rightarrow Cl_2 + 2NH_3$$

Ammonia dissolves in water to form ammonium hydroxide:

$$NH_3 + H_2O \rightarrow NH_4OH$$

Once dissolved, it dissociates as follows:

$$NH_4OH \rightarrow NH_4^+ + OH^-$$

The degree of dissociation is pH dependent. The pH dependence of monochloramine dissociation can then be demonstrated in the following overall reaction:

$$2NH_2Cl + 2H^+ + 2H_2O + 2e^- \rightarrow OCl^- + Cl^- + 2NH_4^+$$

As opposed to chlorine, the cathodic reaction with monochloramine results in a localised increase in pH through proton removal. A more detailed description will be given later in this document with respect to the oxidation potential of monochloramine and its pH dependence.

Various other oxidising reactions can take place in the absence of oxygen, chlorine or monochloramine at the cathode. Typical examples are ferric ions in solution, dissolved hydrogen, sulphate and nitrate. Of these reactions, only reactions with dissolved hydrogen are significant for this discussion.

The hydrogen half reaction is as follows:

$$2H^+ + 2e^- \rightarrow H_{2(g)}\uparrow$$

This reaction is favoured under strictly anaerobic conditions at a low pH. More will be said about this reaction later in this document.

2.5 Corrosion mechanism

Some of the chemical reactions that are typically observed at the cathodic and anodic reaction sites have been outlined in the previous section. This reaction schemes form the basis of various corrosion models that have been developed to explain the observations when iron corrodes. However, before an attempt can be made to describe the relevant corrosion models, it is important to give a brief overview of the general mechanism of the corrosion of iron. This discussion is based primarily on the outlines given by Fontana (1987) and Atkins (1984). For a more detailed and fundamental discussion, the interested reader is advised to consult these or any other related textbooks.

In the first part of discussion, thermodynamic principles are discussed. Electrode kinetics is discussed in the latter part of this section.

2.5.1 Thermodynamics

The electro-motive force (emf) of a system is dependent on the concentrations of the species that are involved in a particular reaction (Atkins, 1984). Consider a cell $A|A^{v+}||B^{v+}|B$ with the following reaction:

$$A + BX \leftrightarrow AX + B \text{ or } A + B^{v+} + X^{v-} \leftrightarrow A^{v+} + X^{v-} + B$$

The respective half-cell reactions for this reaction are:

Right: $B^{v+} + ve^- \leftrightarrow B$ $\qquad E_R$
Left: $A \leftrightarrow A^{v+} + ve$ $\qquad E_L$

The potential difference across electrode-electrolyte interfaces are given by the following expression:

$$\Delta\phi = \Delta\theta^{\theta} - \frac{RT}{vF}\ln\left\{\frac{a(reduction - species)}{a(oxidative - species)}\right\}$$

The overall emf of the cell is given by the so-called Nernst-equation:

$$\begin{aligned} E &= E_R - E_L \\ &= E^\theta - \frac{RT}{\nu F}\ln\left\{\frac{a(A^{\nu+})a(B)}{a(A)a(B^{\nu+})}\right\} \end{aligned}$$

The emf of the cell is zero when all the reagents are at their equilibrium concentrations:

$$0 = E^\theta - \frac{RT}{\nu F}\ln\left\{\frac{a(A^{\nu+})a(B)}{a(A)a(B^{\nu+})}\right\}$$

$$E^\theta = +\frac{RT}{\nu F}\ln\left\{\frac{a(A^{\nu+})a(B)}{a(A)a(B^{\nu+})}\right\}$$

The equilibrium constant, K, for the cell is as expressed as follows:

$$\begin{aligned} K &= \left\{\frac{a(A^{\nu+})a(X^{\nu-})a(B)}{a(A)a(B^{\nu+})a(X^{\nu-})}\right\}_e \\ &= \left\{\frac{a(A^{\nu+})a(B)}{a(A)a(B^{\nu+})}\right\}_e \end{aligned}$$

Therefore, the standard emf of the cell and the equilibrium constant is related as follows:

$$E^\theta = \frac{RT}{\nu F}\ln K$$

or

$$K = \exp\left(\frac{\nu F E^\theta}{RT}\right)$$

The standard free energy change, ΔG^θ, and the standard electrode potential, E^θ, is related through the expression:

$$\Delta G_m^\theta = -RT\ln K$$

and therefore

$$\Delta G_m^\theta = -\nu F E^\theta$$

The emf, E, at any arbitrary composition results to a corresponding change in free energy, ΔG_m:

$$\Delta G_m = -\nu FE$$

The importance of this relationship is that the measurements of emf can provide information on the thermodynamic aspects of a reaction. Knowledge of the thermodynamic properties can allow one to estimate the emf under certain conditions. One such example is the temperature dependence of E. The variation of ΔG with temperature is expressed as follows:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

therefore

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S_m}{\nu F}$$

The change in free energy is related to the enthalpy change, temperature and entropy, ΔS, change of the reaction through the following expression:

$$\Delta G = \Delta H - T\Delta S$$

therefore, the enthalpy, ΔH, change is again related to the emf in the following manner:

$$\begin{aligned}\Delta H &= \Delta G + T\Delta S \\ &= -\nu F\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right]\end{aligned}$$

The standard values for emf, enthalpy and entropy of reactions and Gibbs functions are all interrelated. This information predicts to what extend a reaction can proceed. If it is thermodynamically not feasible, no reaction is possible. This is the underlying principal that serves as a driving force for the reaction in one or other direction.

2.5.2 Corrosion kinetics

A corroding system is certainly not at equilibrium. It is important to understand the factors that play a roll in determining the corrosion rate in order to control and limit losses.

During corrosion, net oxidation and reduction reactions take place at the anodic and cathodic sites. It implies that the potentials at these sites are no longer at their equilibrium values. The deviation from the equilibrium potential is called *polarization* and is a result of the net current. The magnitude of polarization is called the *overvoltage*. The overvoltage, η, is a measure of polarization with respect to the equilibrium potential of an electrode. The value of the overvoltage is zero at the equilibrium value and is expressed in terms of volts or millivolts plus or minus the zero reference. Therefore, $\eta = E - E^0$.

Consider the half-reaction for dissolved oxygen under neutral or alkaline conditions:

$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$ $\qquad E^0 = 0{,}401$ V

At equilibrium, the forward and backward reaction rates are equal, namely $r_{oxid} = r_{red}$. Although there is no net current, there is a fixed rate of exchange of current in both directions. The relationship between the reaction rate and current density can be expressed in terms of Faraday's law:

$$r_{oxid} = r_{red} = \frac{i_0}{zF}$$

At zero overvoltage the current density equals, i_0, also referred to as the *exchange current density*. Exchange current density, i_0, is the rate of oxidation and reduction reactions at an equilibrium electrode expressed in terms of current density. This value is determined by a large number of factors such as the nature of the metal electrode, the composition of the dissolved electrolytes, the ratio of the oxidized and reduced species and temperature. For this reason it must be determined experimentally for each system.

Electrochemical polarization can be classified broadly into two main types, namely <u>activation</u> and <u>concentration polarization</u>. The former refers to a situation where the overall rate of sequential electro-chemical reactions is controlled by a slow step. The relationship between reaction rate and overvoltage for activation polarization is:

$$\eta_a = \pm\beta \log\frac{i}{i_0}$$

This principal is demonstrated in figure 2.4. The reaction rate of an electro-chemical reaction is very sensitive to any change in the electrode potential.

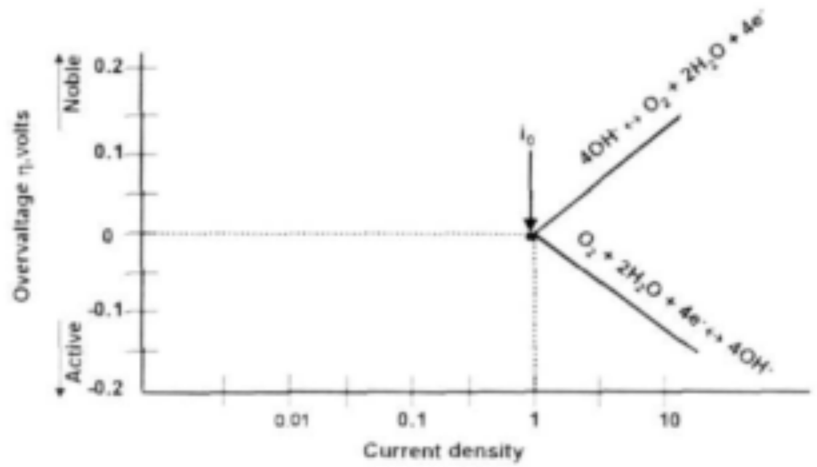


Figure 2.4 *Activation-polarization curve of an oxygen electrode*

Concentration polarization is observed when the corrosion rate is limited as a result of the diffusion rate of a reactant to the electrode surface. This limiting rate is called the limiting diffusion current density, I_L. It is the maximum possible oxidation or reduction rate for a system operated under specific conditions. i_L can be expressed by the following relationship:

$$i_L = \frac{DzFC_B}{x}$$

where D is the diffusion constant for a reacting species in the bulk solution, C_B its concentration, χ the diffusion film thickness and the other parameters as defined earlier. There is therefore a direct relationship between the concentration of the reagent and the limiting diffusion current density and an inverse relationship with the diffusion film thickness. The diffusion film thickness is typically reduced at higher agitation intensities.

In the absence of activation polarization, the expression for concentration potential, η_c, is simplified as follows:

This expression clearly demonstrates the maximum limit for corrosion as the current density approaches the limiting value. This is graphically illustrated in figure 2.5.

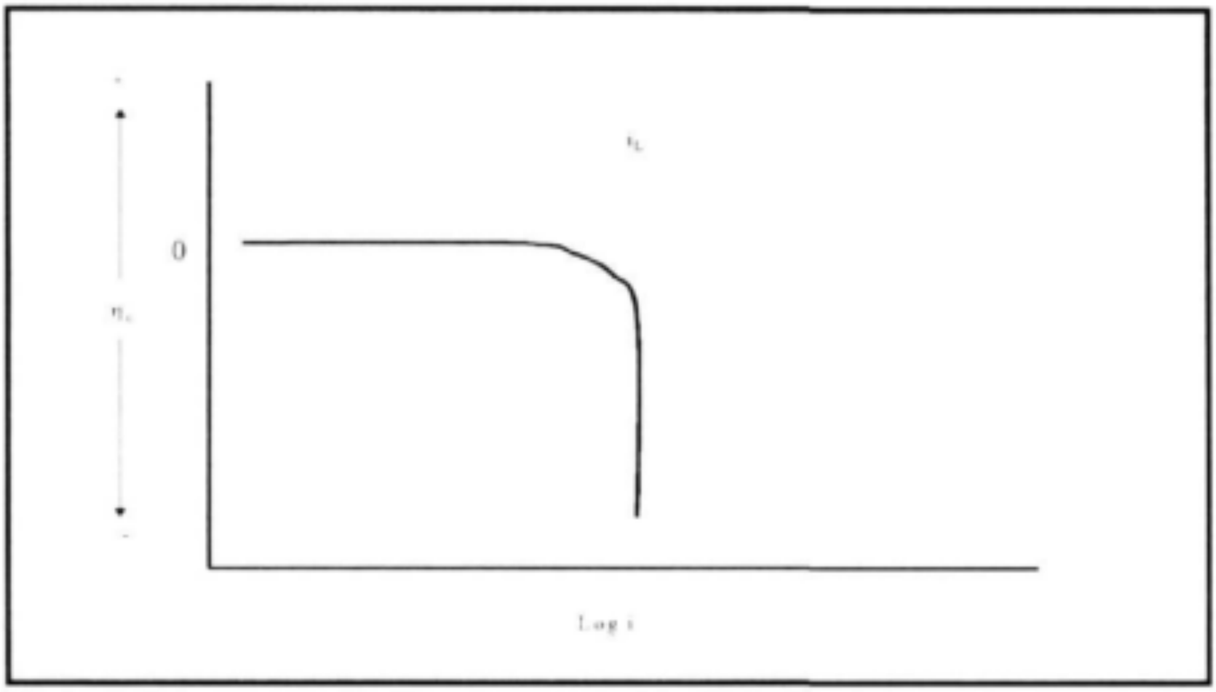


Figure 2.5 *Concentration polarization curve for a reduction process (redrawn from Fontana (1987)*

$$\eta_c = 2.3\frac{RT}{zF}\log\left(1-\frac{i}{i_L}\right)$$

It is typically observed that activation polarization dominates at relatively low corrosion rates. At higher corrosion rates the transport of reagents to the electrode surface is dominated by diffusion and consequently concentration polarization determines the overall rate. The overall polarization of the electrode is therefore the sum of the contribution of both activation and concentration polarization and is expressed as follows:

$$\begin{aligned}\eta_T &= \eta_a + \eta_c \\ &= \pm\beta\log\frac{i}{i_0} + 2.3\frac{RT}{zF}\log\left(1-\frac{i}{i_L}\right)\end{aligned}$$

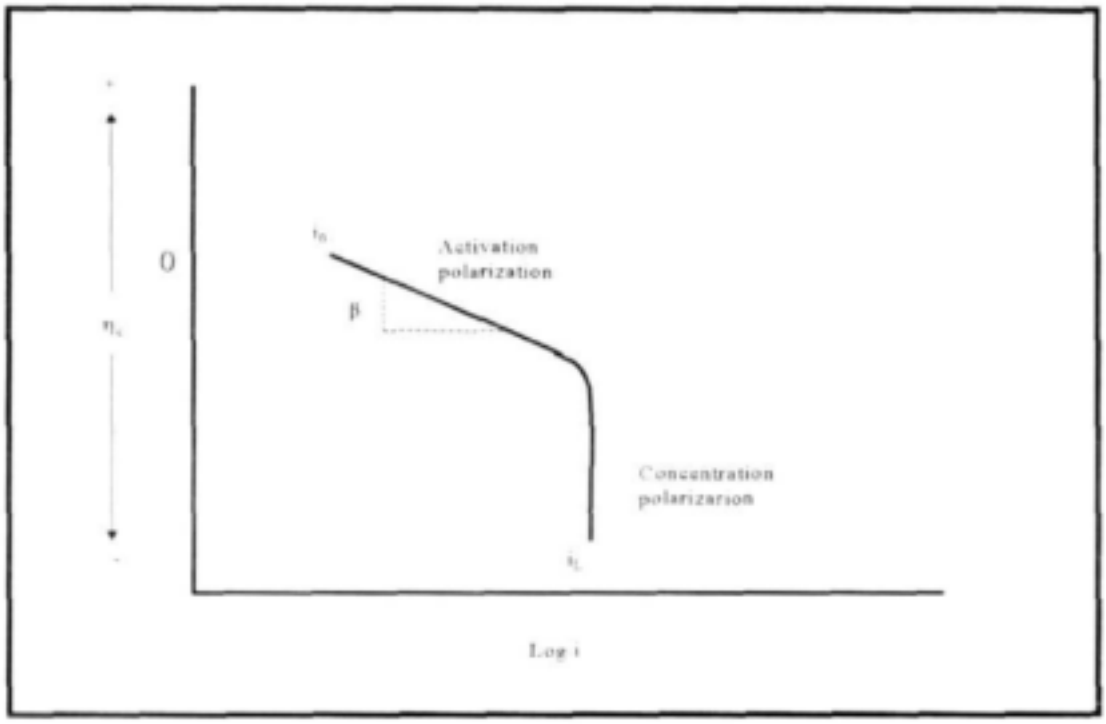


Figure 2.6 *Combined polarization curve for activation and concentration polarization for a reduction process (redrawn from Fontana (1987)*

However, at the anode where metal ions enters the bulk fluid as a result of dissolution, the concentration of the ions is so high that diffusion limitation does not play any role. Therefore, anodic dissolution is only expressed in terms of activation polarization, namely:

$$\eta_{diss} = \beta \log \frac{i}{i_0}$$

The cathodic reaction (reduction) can then be expressed by the following relationship:

$$\eta_{red} = -\beta \log \frac{i}{i_0} + 2.3 \frac{RT}{zF} \log\left(1 - \frac{i}{i_L}\right)$$

The last two equations form the bases for the calculation of all electro-chemical reactions. However, where metals demonstrate active-passive behavior, there is a significant deviation from the dissolution expression at the cathode. Iron is a typical example.

Passivation can be explained in terms of a general reaction scheme presented by Atkins (1984).

$$M^+ + e^- \leftrightarrow M$$
$$MX \leftrightarrow M^+ + X^-$$

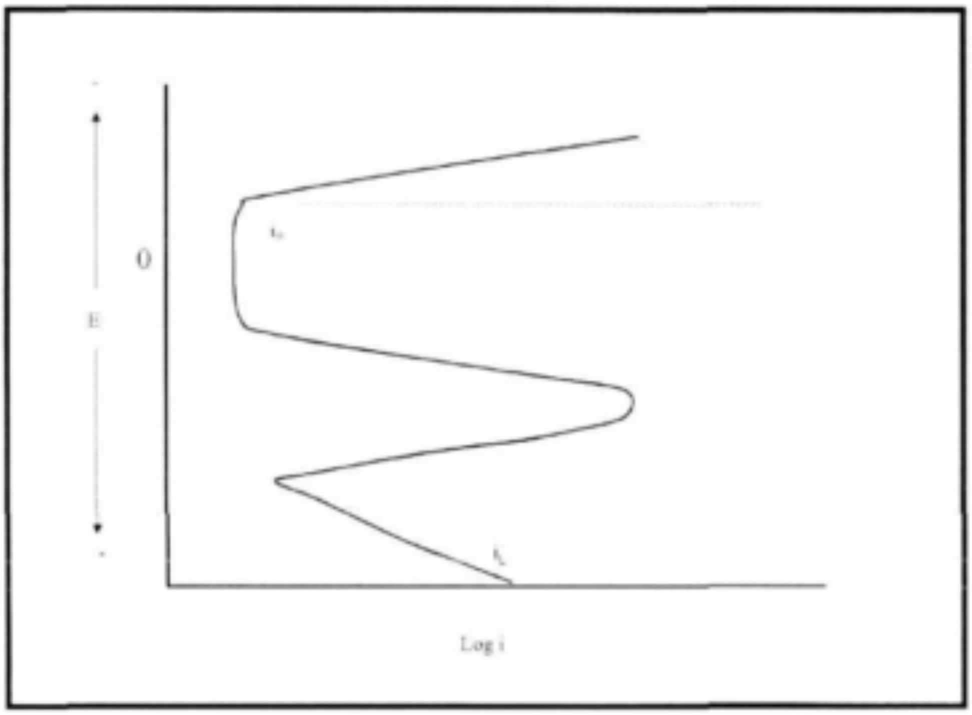


Figure 2.7 *Passivation of mild steel at different applied potentials (redrawn from Fontana (1987))*

Therefore

$$MX + M^+ + e^- \leftrightarrow M + M^+ + X^-$$
$$MX + e^- \leftrightarrow M + X^-$$
$$\mu_{MX} + \mu_{e^-}(M) \leftrightarrow \mu_M(M) + \mu_{X^-}(S)$$

If it is assumed that ferrous hydroxide is the first precipitate that forms on the mild steel surface, the reaction scheme can be applied as follows:

$$Fe(OH)_2 \leftrightarrow Fe^{2+} + 2OH^-$$
$$Fe(OH)_2 + Fe^{2+} + 2e^- \leftrightarrow Fe^{2+} + Fe + 2OH^-$$
$$Fe(OH)_2 + 2e^- \leftrightarrow Fe + 2OH^-$$

where

$$\mu_{Fe(OH)2} + \mu_{e^-}(M) = \mu_{Fe}(M) + \mu_{OH^-}(S)$$

$$pe^- = pK_{eq} + pH - 14$$

An overview of some of the known general properties of monochloramine and sodium silicate are be given to demonstrate its possible role in the overall kinetics of the corrosion of mild steel.

LeChâvelier demonstrated that for copper and PVC pipe surfaces, the application of free chlorine residual results in greater biofilm inactivation as compared with a similar dose of monochloramine. The opposite is observed for a galvanized pipe surface where the application of monochloramine results in greater inactivation than did free chlorine. During the same studies, it has also been demonstrated that the free chorine demand was ten times higher for the galvanized pipe surface as compared with the copper and PVC pipe surfaces. The reason for this difference, as explained by LeChâvelier, is the accumulation of corrosion products with a high chlorine demand, such as ferrous ions, within the film on the galvanized pipe surface. Monochloramine, as suggested, does not react with the corrosion products and is then available to react solely with the compounds of the biofilm (Chou and Suffet, 1991).

It is unlikely that monochloramine does not react and oxidize corrosion products. This observation is better explained if it is assumed that the metal surface is passivated by monochloramine and thereby reduce the corrosion rate. The lower corrosion rate (cathodic reaction) will result in a lower demand for monochloramine while less corrosion products will be formed. The overall demand for monochloramine will be significantly lower. The decay rate of monochloramine in the reticulation network will therefore be less and it will retain its bacteriostatic nature for much longer periods.

2.5.3 Corrosion model

The overall corrosion reaction is the sum of the half reactions at the anode and the cathode (Loewenthal *et al.*, 1986). When oxygen is the electron acceptor, it can be written as follows:

$$2Fe_{(s)} + O_2 + 4H^+ \leftrightarrow 2Fe^{2+} + 2H_2O$$

The rate of the reaction is limited by the slower reaction of the two and can therefore either be anodic or cathodic controlled. Loewenthal *et al.* (1986) gave a comprehensive overview of some of the factors that may determine whether the reaction is controlled at the anode or at the cathode. Below follows a brief summary of some these factors.

When mild steel is exposed to distilled water the overall reaction is governed by the rate of oxygen supply. When the rate of supply is low, the cathodic reaction is low and dictates the rate of the anodic reaction, namely the rate of formation of $Fe(OH)_2$. Under these conditions, the rate of oxidation $Fe(OH)_2$ to iron oxide is even much slower than the rate of formation of $Fe(OH)_2$. $Fe(OH)_2$ therefore displaces any metal oxides that may form at the metal surface and no metal oxide film is formed. When the rate of oxygen supply is low, $Fe(OH)_2$ and

$Fe(OH)_3$ form so rapidly that tertiary corrosion products can not be formed at the corroding surface. No protection can be achieved which results in "red water" problems at low pH or tubercule formation at high pH values.

In buffered water, carbonates are formed at the cathode as a result of the localized pH increase. When the solubility product for calcium carbonate is exceeded it will form a permeable precipitate. Since the cathodic area will be limited it will also limit the cathodic reaction. At the reduced rates, tertiary corrosion products will form at the anode. The anodic area will finally be covered and no further reaction will be possible and complete passivation will be achieved. Anodic control is therefore only possible if the cathodic reaction can be reduced sufficiently to allow the formation of tertiary corrosion products.

Loewenthal *et al.* (1986) gave an overview of the most important factors that may control the overall rate, namely dissolved oxygen concentration, velocity of flow, calcium and carbonate species concentrations in the bulk solution, buffer capacity and influence of organic material on the nature of $CaCO_3$ precipitate, chloride and sulphate concentrations.

CHAPTER 3

3. CHEMISTRY OF MONOCHLORAMINE AND SODIUM SILICATE

3.1 Introduction

An overview of some of the known general properties of monochloramine and sodium silicate are given in this chapter to demonstrate their potential role in the overall kinetics of mild steel corrosion.

3.2 Chemistry of Monochloramine

LeChâvelier demonstrated that for copper and PVC pipe surfaces, the application of free chlorine residual result in greater biofilm inactivation as compared with a similar dose of monochloramine. The opposite is observed for a galvanized pipe surface where the application of monochloramine results in greater inactivation than free chlorine. During the same studies, it was also demonstrated that the free chlorine demand for the galvanized pipe surface was ten times higher as compared with the copper and PVC pipe surfaces. The reason for this difference, as explained by LeChâvelier, is the accumulation of corrosion products with a high chlorine demand, such as ferrous ions, within the film on the galvanized pipe surface. Monochloramine, as suggested, does not react with the corrosion products and is then available to react solely with the compounds of the biofilm (Chou *et al.*, 1991).

It is most likely that monochloramine reacts and oxidizes corrosion products. This observation is better explained if it is assumed that monochloramine passivates the metal surface and thereby reduce the corrosion rate. The lower corrosion rate (cathodic reaction) will result in a lower demand for monochloramine while less corrosion products will be formed. The overall demand for monochloramine will be significant lower. The decay rate of monochloramine in the reticulation network will therefore be less and it will retain its bacteriostatic nature for much longer periods.

3.3 Chemistry of Sodium Silicate

In his review of the work of Stericker, Wood, Beecher and Laurence (1957) gave the following summary:

- Ionic or crystalloid silica gives a characteristic colour reaction with ammonium molybdate and has marked corrosion-inhibitive properties
- Stable hydrated colloidal silica does not react to the molybdate colour test and is an better inhibitor than crystalloid silica
- Unstable hydrated colloidal silica is negative to the colour test and is a poor corrosion inhibitor. Unlike crystalloid and stable hydrated forms, this material may form gels or gelatinous precipitates on standing
- Unhydrated silica does not give color reaction and does not form gels but may settle out on standing. It has no influence on corrosion.

Wood *et al.* (1957) conducted a series of experiments with metal specimens exposed in several industrial cooling systems to test the corrosion-inhibiting effect of ionic or crystalloid silica. Based on his observations, they concluded that crystalloid silica is highly effective in stopping corrosion of mild steel in contact with a wide variety of industrial cooling waters. Crystalloid silica at 30-to 40 mg/ℓ provided adequate protection in waters containing more than 500 mg/ℓ chlorides and sulphates. It seems as though pH values of 8.6 and higher have an adverse effect, which may be corrected by adjusting the pH with mineral acids. Magnesium hardness in access of 250 mg/ℓ, expressed as $CaCO_3$ greatly reduces the inhibitive action. The authors also concluded that it is necessary to have an initial coating of corrosion products before crystalloid silica can act as a corrosion inhibitor. It therefore indicates that sodium silicate will be effective in systems in which corrosion is active prior to the application of treatment. Shuldener and Sussman (1960) confirmed the observation.

Lahodny-Šarc *et al.* (1981) demonstrated that the corrosion-inhibiting effect could be related to the anodic character of sodium silicate instead of the alkalinity of the solution. The same authors also indicated that the precipitation of an amorphous iron hydroxide as a corrosion product and its further crystallization may be highly influenced by the presence of silica added as sodium silicate. The following reaction scheme, where sodium hydroxide reacts with either dissolved ferrous- or ferric hydroxide, demonstrates this principal:

$$Fe(OH)_2 + Na_2SiO_3 \leftrightarrow FeSiO_3 + 2NaOH$$

or

$$Fe(OH)_3 + Na_2SiO_3 \leftrightarrow FeSiO_3(OH) + 2NaOH$$

When this complex is formed, iron hydroxide does not precipitate. It is kept in solution instead. This serves as the basis for controlling staining of clothes and household equipment and metallic taste in groundwater sources contaminated with dissolved ferrous ions. When sodium silicate is administered in unaerated groundwater, a strong iron complex is formed with silicate. The water is then suitable for domestic purposes (Joseph Crosfield and Sons (ref SS2-12)).

Joseph Crosfield and Sons (ref SS2-9) explained that sodium silicate reacts with corrosion products of the metal to form an almost insoluble protective film of metal silicate. The rate of formation of the protective film is dependent on the type of metal being treated and is probably influenced by the rate of oxidation of the particular metal. With iron and steel, the process is relatively slow as compared with metals such as lead and aluminium. Shuldener, *et al.* (1960) speculated that, once iron oxides are formed, silicate precipitates these in a film on the surface of the piping as fast as formed. It therefore explains the effectiveness of silicate treatment in overcoming red water problems.

Briggs (1974), Shuldener *et al.* (1960) and Joseph Crosfield and Sons (ref SS2-9) reported that the mechanism involved in building up an almost unreactive layer imparts three important advantages to the system in that:

- Build-up of thick deposits is prevented as the metal surface is sealed and not available to react further with the sodium silicate.
- The whole of a very extensive water system can be treated from one point, protection gradually radiating from the point of dosing.
- After initial protection has been achieved by applying 10 mg/ℓ sodium silicate, only small continuous doses of sodium silicate, in the order of 4 mg/ℓ, are necessary to repair any loss or damage to the protective film.

White *et al.* (1986) gave a more comprehensive explanation of the possible mechanism of the inhibitive action of silicates. It is thought that the formation of a siliceous film on the metal surface is related to the hydrolysis of silicates to form colloidal particles. Silica or complex silicic ions of the general formula $(mSiO_2.nH_2O.pSiO_3^{2-})^{2p-}$, are negatively charged particles. Since the anodic areas are positively charged, the negatively charged particles migrate towards to these areas where it is concentrated on the metal surface. As the local concentration exceeds the solubility limit, the particles coalesce into larger and larger aggregates and finally cover the surface with a gel like film. The colloidal gel has a porous structure that is permeable to ions migrating through it and therefore has no corrosion-inhibiting properties. When it is "mixed" with corrosion products, the permeability decreases and corrosion ceases. It is speculated that the corrosion protection is a combination of silica gel formation combined with an insoluble iron product such as ferric hydroxide or ferrosilicate. Once the hydrous metal oxide or metal silicate has been covered with a layer of silica, corrosion ceases.

This is probably better explained by Stumm and Morgan (1981) in their discussion of the surface chemistry of oxides, hydroxides and oxide minerals. They pointed out that most of the solid phases in natural waters contain oxides or hydroxydes of elements such as Si, Al and Fe. Interactions of cations and anions with hydrous oxide surfaces play a significant role in water systems, geochemical processes and colloid chemistry. Metal or metalloid oxides are generally covered with surface hydroxyl groups in an aqueous medium. Such a hydroxylated oxide particle can be regarded as a polymeric oxoacid or –base. The adsorption of protons or hydroxyl groups, cations, anions and weak acids can be described in terms of surface co-ordination reactions at the oxide-water interphase. The proton transfer at the amphoteric surface of metal or metalloid hydrous oxides determines the surface charge and is therefore pH-dependent.

This charge corresponds to the difference in the protonated and deprotonated metal hydroxide (≡MeOH) groups. Protons and metal ions are Lewis acids while hydroxyl and other bases are Lewis bases. The OH group on a hydrous oxide surface has a complex-forming O-donor group like an OH^- or an OH group attached to elements such as silicate, polysilicate or phosphate. The protons and metal ions is therefore exchanged at the co-ordinating surface sites:

$$\equiv MeOH + M^{z+} \leftrightarrow \equiv MeOM^{(z-1)} + H^+$$

In a similar manner, OH^- is displaced from the surface by co-ordinating anions in a process known as ligand exchange:

$\equiv Me\text{-}OH + A^{z-} \leftrightarrow MeA^{(z-1)} + OH^-$

The specific binding of H^+ and cations increases the net charge of the particle surface. Similarly, the specific binding of OH^- and anions decreases the net charge of the particle surface. The extent of adsorption and the net surface charge of an oxide particle is a function of pH and the activity of cations or anions in solution. The extent of adsorption of anions and of weak acids and its pH-dependence can be explained by considering the affinity of the surface sites for the ligands and the acid-base properties of the surface sites and those of the ligands. One such example is the effect of silisic acid on the surface charge of goethite (α-FeOOH). At a pH less than 9, dissolved silica is present as H_4SiO_4. During the adsorption, protons are released through the following reactions and the net surface charge of goethite is lowered:

$\equiv FeOH + H_4SiO_4 \leftrightarrow \equiv FeOSi(OH)_3 + H_2O$
$\equiv FeOSi(OH)_3 \leftrightarrow \equiv FeOSiO(OH)_2^- + H^+$

Based on this discussion, it can be seen that the adsorption of silicate is determined by the affinity and availability of the surface sites and the solute concentration of the ligands.

White *et al.* (1985) conducted a series of experiments to test the effect of sodium silicate in the presence of high magnesium concentrations and a high alkalinity medium. They observed that the magnesium concentration has a definite effect on the corrosion-inhibiting effect of sodium silicate. Based on their observations, they postulated that magnesium carbonated first forms an unstable layer close to the surface of the metal. This layer of magnesium carbonate is covered by a semi-porous silicate colloidal gel. Local carbonate dissolution then leads to the formation of pits.

It can therefore be concluded that sodium silicate will act as a corrosion inhibitor under certain conditions. The degree of adsorption is a function of pH and sodium silicate concentration. Since it reacts with various corrosion products, the rate of corrosion is important. If the corrosion rate is high, it may react with ferrous or ferric ions before it precipitate as hydroxides. It will therefore control "red water", but not the corrosion rate. Once the precipitates are formed and in suspension, it may adsorp on the surfaces of the particles with no effect on the corrosion rate at all. If, however, the conditions are right for the formation of tertiary corrosion products, silicic acid will be absorped on the surface of the material and form a stable metal silicate layer dense enough to prevent further migration of cations or anions through the protective film. If new anodic sites then appear, ferrous or ferric hydroxide will then be adsorped and further corrosion be inhibited.

CHAPTER 4

4 EXPERIMENTAL PROCEDURES

4.1 Introduction

The weight loss experiments and electro-chemical corrosion measurements were done separately. The experimental procedures used for each set of experiments are discussed separately.

The chemical analysis was performed using the same procedures for each set of experiments and references to the methods are given.

4.2 Weight loss experiment

4.2.1 Experimental set-up

Experimental loops for this project consisted of nine separate, but identical systems. Each consisted of one corrosion cell containing ten mild-steel coupons, in the form of a short pipe, 40 mm long and 12,5 mm in diameter, for the weight-loss corrosion tests, a pump, rotameter and a 200-litre tank, connected in series. The water was recycled continuously through the system at a pumping rate of between 600 and 900 ℓ/h, corresponding to linear velocities of between 1,36 to 2,04 m/second through the pipe coupons.

Figure 4.1 *Picture showing some of the nine experimental loop systems used.*

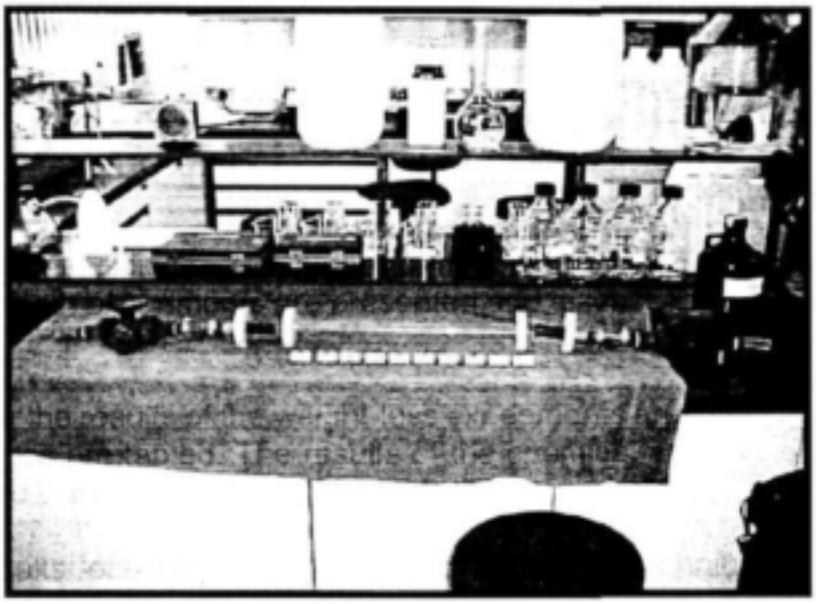


Figure 4.2 *Picture of the coupon cell*

The coupons were cut from standard mild steel rod to an internal nominal diameter of 12,5 mm. The standard length of a coupon were 40 mm. The ends of the coupons were lathe-cut to ensure a smooth, flat finish to seal tightly against the gaskets that separated the coupons. After machining the surfaces, the coupons were degreased by means of acetone to remove cutting oil, polished and given an exterior coating of an oil-based paint to protect them during handling and to prevent exterior moisture-induced corrosion. Paint was applied to the butt ends as well. Care was taken not to cover the internal surface of the coupons with paint.

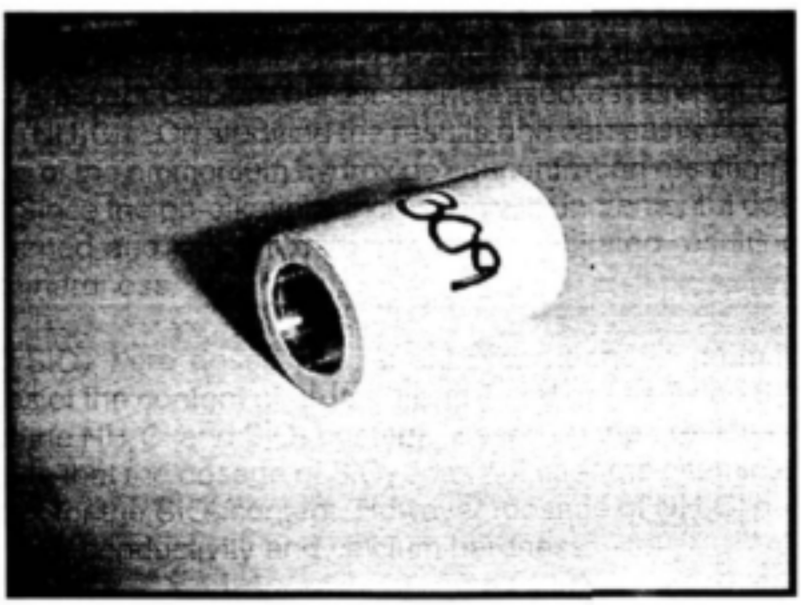


Figure 4.3 *Fresh coupon.*

The aim of this experiment was to determine both short-term and long-term weight losses, i.e., the cumulative loss of metal over an extended period of exposure. **Short-term weight-loss measurement** involved the weekly removal of an exposed coupon from a test loop for a period of four weeks. **Long-term weight-loss measurements** is usually done by exposing coupons in a test loop for one, two, three, four and five months. It was decided, however, to remove the coupons weekly for the first seven weeks and thereafter on the eleventh, thirteenth, fifteenth, eighteenth, twentieth and twenty-second week. In this manner, both short-term and long-term objectives were met.

The exposed coupons were replaced with fresh mild-steel coupons and subsequently dried, prepared and weighed The corrosion rates were expressed in terms of µm/year.

An attempt was made to use rectangular mild steel plate coupons in the same experimental set-up. After a short while, it was observed that the corrosion rate was high, that too much corrosion products were formed and that the water in the 200 litre drums had to be replaced often due to a build up of dissolved or suspended corrosion products in the water. There was a concern that it may influence the experimental results and it was finally decided to remove it. The lower linear flow rate over the plate coupons seemed to have accelerated the corrosion rate.

4.2.2 Water

Each of the 200 litre drums was filled with carbonated, chemically stable, filtered water prior to disinfection with chlorine. This water was slightly scale forming with a calcium carbonate precipitation potential of more or less 2 mg/ℓ as $CaCO_3$. The pH typically varied between pH 8-8.4.

The quality of the water in the experimental set-up was checked daily, except over week-ends and holidays but no more than one day was ever skipped. The samples were analysed for parameters such as temperature, conductivity, pH, alkalinity, calcium and total hardness, total iron, silicate and monochloramine. The dissolved oxygen concentration was also measured for a period of ten weeks until the instrument failed. The oxygen concentration varied between 86% and 98% saturation with the higher saturation levels during the initial cooler periods. The temperature varied between 20°C and 25°C while the atmospheric pressure remained constant at 0.85 atm.

Sodium silicate ($NaSiO_3$) as a source of silicate (SiO_2) and monochloramine solutions were carefully prepared in the laboratory and dosed at a rate to maintain a fixed residual of each respective compound in the separate drums. The concentrations of the respective additives were as follows:

Drum 1	0.5 mg/ℓ monochloramine
Drum 2	1.0 mg/ℓ monochloramine
Drum 3	3.0 mg/ℓ monochloramine
Drum 4	5.0 mg/ℓ sodium silicate as SiO_2
Drum 5	10 mg/ℓ sodium silicate as SiO_2
Drum 6	15 mg/ℓ sodium silicate as SiO_2
Drum 7	0.5 mg/ℓ monochloramine + 15 mg/ℓ sodium silicate as SiO_2
Drum 8	3.0 mg/ℓ monochloramine + 5.0 mg/ℓ sodium silicate as SiO_2
Drum 9	no additives-filtered water

The water was initially replaced once a week but later only when there was a build up of corrosion products and compounds that could have affected the alkalinity of the water.

4.3 Rapid scanning techniques experimental set-up

4.3.1 Experimental set-up

Bench-scale tests were performed, using the Schlumberger 1286 Electrochemical Interface apparatus in combination with the Corrosoft ERIC program after completion of the weight-loss experiments. The same conditions for the nine drums described above were maintained.

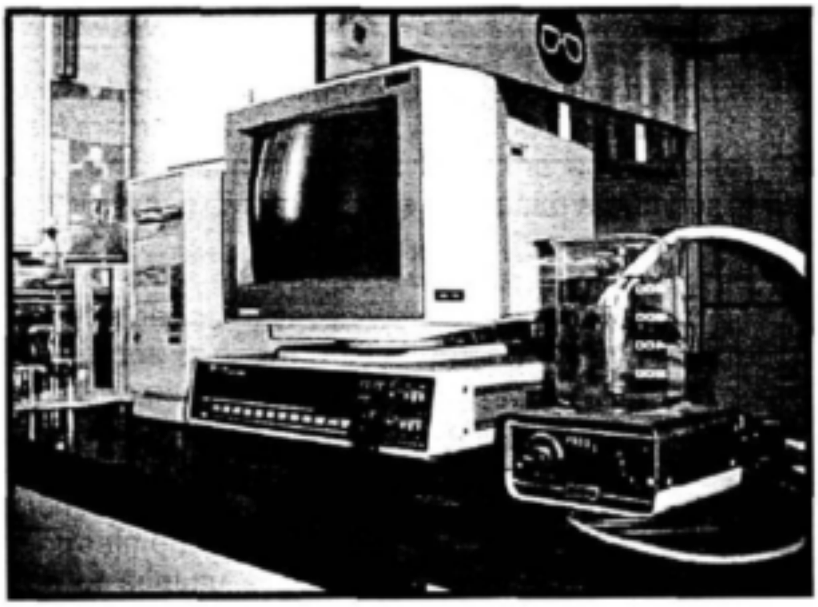


Figure 4.4 *Sclumberger Model 1286 Electrochemical Interface Apparatus and computer loaded with Corrosoft ERIC Program*

The objective of the rapid scanning was:

1. To verify the optimum dosages of either sodium silicate and monochloramine;
2. To select the optimum pH for corrosion inhibition for the two chemicals (especially for sodium silicate);
3. To test any difference in the initial corrosion rate when the raw water is treated with different coagulants;
4. To identify the corrosion mechanism;
5. To identify the mechanism of inhibition by chloramination and application of sodium silicate.

Experimental loops for this project consisted of nine separate, but identical systems. Each consisted of two sets of mild-steel electrodes in a container for the electro-chemical tests, a pump, a rotameter and a 200 litre tank, connected in series. The water was recycled continuously through the system at a pumping rate of between 600 and 900 ℓ/h, whereby turbulence was created in the electrode chamber to ensure that the corrosion was not diffusion limited.

Figure 4.5 *Typical example of corroded mild steel electrodes with graphite auxiliary electrodes*

4.3.2 Water

Exactly the same conditions were maintained as described above for the weight-loss experiments.

4.3.3 Electro-chemical measurements

The 1286 Electrochemical Interface (1286 ECI) Apparatus was used with a Corrosoft ERIC program supplied by Capcis in the United Kingdom. The 1286 ECI and ERIC program were used to obtain Tafel plots from which corrosion rates were calculated. The apparatus controls the direct current (DC) characteristics of an electrochemical cell. Tafel plots are performed by polarising the mild steel specimen about 500 mV cathodically and anodically from the corrosion potential or zero overvoltage, E_{corr}. E_{corr} is the potential of a specimen where the anodic and cathodic currents are equal in magnitude. The 1286 ECI measures the corresponding current as it changes the potential on the metal surface, relative to a reference electrode, from 500 mV below E_{corr} to 500 mV above E_{corr}. The sweep and plot functions setting used with the ERIC program are given in Table 4.1 (Brits *et al.*, 1998).

Table 4.1 Sweep and Plot function settings (after Brits *et al.*, 1998)

Sweep Mode	***Potentiostatic***
Plot Mode	log(i)/E
Sweep limit (1)	-500 mV
Sweep limit (2)	+500 mV
Number of sweep segments	One
Sweep rate	1V/min
Sweep time	1.25 min
Datum	Ecorr
Emin	-500 mV
Emax	+500 mV
Imin	1 μA
Imax	1 A
Hold time at start of sweep	10 min
Electrode area	1.12 cm^2

CHAPTER 5

5. EXPERIMENTAL RESULTS

5.1 Introduction

The results of sodium silicate ($NaSiO_3$) and monochloramine (NH_2Cl) dosing on the water quality for both experiments are presented and discussed in the first part of this chapter.

Followed by that, the results of the weight-loss experiments are shown graphically and some of the values are tabled. The results of the chemical analysis of the corrosion products are also presented.

Finally, the results obtained with the rapid scanning technique are presented graphically.

5.2 Sodium silicate and monochloramine dosing and the water quality

The results of the regular chemical analysis done on the water samples of all the drums throughout the duration of both experiments are presented respectively in tables 5.1 and 5.2.

When the parameters for drums 4, 5 and 6 are compared with the control, drum 9, all the parameters but dissolved SiO_2 remained unchanged. It can therefore be concluded that any changes in corrosiveness of the medium can be contributed to the effect of dissolved SiO_2.

When the parameters of drums 1,2 and 3 are compared with that of drum 9, there is a notable difference in the conductivity, pH, pp- and total alkalinity and calcium hardness. All the parameters accept calcium hardness increased as a result of the addition of monochloramine (NH_2Cl). On studying the results one can easily conclude that there is a gradual build-up of the ammonium hydroxide concentration resulting in an increase in the pp-alkalinity. Since the pp-alkalinity increased with incremental dosages, the water is eventually softened and calcium carbonate is precipitated resulting in decreasing values of calcium hardness.

Both NH_2Cl and SiO_2 were dosed in different proportions in drums 7 and 8. The chemical analyses of the content of drums 1 and 7 and drums 3 and 8 respectively are similar accept for the NH_2Cl and SiO_2 content. Based on the previous discussion, one can again conclude that the dosage of SiO_2 does not alter the chemical composition of the medium except for the SiO_2 content. However, dosage of NH_2Cl has a direct effect on the alkalinity, pH, conductivity and calcium hardness.

Table 5.1 Chemical analysis of water in the drums during the weight-loss experiment

Parameter		*Drum 1*	*Drum 2*	*Drum 3*	*Drum 4*	*Drum 5*	*Drum 6*	*Drum 7*	*Drum 8*	*Drum 9*
Temperature	Average	22.1	22.7	22.8	22.9	23.1	23.2	23.2	23.0	22.8
	STDev	2.62	2.70	2.80	2.90	2.80	2.90	2.70	2.68	2.77
Conductivity	Average	31.3	36.6	49.0	21.6	22.6	22.2	35.83	45.2	21.1
	STDev	6.98	7.90	15.4	3.80	3.70	3.50	6.89	14.32	3.81
pH	Average	8.04	8.50	8.90	8.30	8.30	8.40	8.59	8.93	8.33
	STDev	0.67	0.50	0.20	0.10	0.10	0.10	0.43	0.19	0.17
pp-Alkalinity	Average	12.0	26.9	73.0	5.40	5.20	5.50	26.9	72.0	4.73
	STDev	13.3	21.2	38.6	5.60	4.70	5.30	17.74	40.32	4.81
Total Alkalinity	Average	90.0	132	231	85.4	87.4	91.6	140	217	80.3
	STDev	59.6	60.6	85.3	19.0	19.0	16.7	51.1	85.3	23.5
Ca-Hardness	Average	64.8	53.9	33.4	60.7	59.8	60.9	53.0	36.8	60.6
	STDev	22.3	20.0	12.9	25.4	24.8	24.5	16.5	12.6	26.3
Mg-Hardness	Average	24.7	26.4	26.2	25.7	27.2	24.9	26.8	27.8	26.8
	STDev	9.9	12.7	12.3	9.9	11.7	13.5	13.14	12.5	10.4
NH_2Cl	Average	0.30	0.70	1.90	0	0	0	0.44	1.70	0
	STDev	0.27	0.4	1.1	0	0	0	0.58	1.16	0
NH_2Cl Dosed	Average	0.19	0.30	1.10	0	0	0	0.23	1.12	0
	STDev	0.22	0.30	1.20	0	0	0	0.26	1.24	0
Total SiO_2	Average	6.16	7.40	7.30	14.6	18.3	23.5	23.9	14.6	6.8
	STDev	3.42	2.70	3.00	3.00	3.00	3.20	2.74	2.09	3.63
Total SiO_2 dosed	Average	0	0	0	4.9	7.0	6.5	5.6	4.2	0
	STDev	0	0	0	2.60	3.70	4.10	2.90	2.53	0
Dissolved Oxygen	Average	6.97	7.00	7.00	7.00	7.00	6.90	7.00	7.05	6.90
	STDev	0.40	0.50	0.40	0.50	0.40	0.40	0.47	0.40	0.46

Summary of chemicals added to the various drums for the weight-loss and rapid scanning tests.

Drum 1	0.5 mg/ℓ monochloramine
Drum 2	1.0 mg/ℓ monochloramine
Drum 3	3.0 mg/ℓ monochloramine
Drum 4	5.0 mg/ℓ sodium silicate as SiO_2
Drum 5	10 mg/ℓ sodium silicate as SiO_2
Drum 6	15 mg/ℓ sodium silicate as SiO_2
Drum 7	0.5 mg/ℓ monochloramine + 15 mg/ℓ sodium silicate as SiO_2
Drum 8	3.0 mg/ℓ monochloramine + 5.0 mg/ℓ sodium silicate as SiO_2
Drum 9	no additives-filtered water

Table 5.2 Chemical analysis of water in drums during rapid scanning experiment

Parameter		*Drum 1*	*Drum 2*	*Drum 3*	*Drum 4*	*Drum 5*	*Drum 6*	*Drum 7*	*Drum 8*	*Drum 9*
Temperature	Average	22.6	22.2	22.8	21.7	21.8	22.2	23.1	22.5	21.9
	STDev	2.8	2.4	2.6	2.5	2.63	2.4	2.5	2.2	2.2
Conductivity	Average	34.4	38.3	39.1	28.4	28.2	28.2	35.7	40.4	28.3
	STDev		8.4	7.62	2.1	1.5	1.7	6.7	7.3	1.4
PH	Average	7.84	8.11	8.87	8.55	8.54	8.53	8.23	8.87	8.57
	STDev	0.77	0.64	0.12	0.06	0.05	0.06	0.38	0.10	0.07
pp-Alkalinity	Average	2.94	6.18	34.6	8.8	6.8	9.5	3.1	32.5	9.9
	STDev	3.9	8.47	11.1	2.8	3.1	3.7	4.5	11.6	2.6
Total Alkalinity	Average	78.6	80.4	169.2	124.6	123.4	122.0	57.1	178	124.3
	STDev	61.1	51.9	29.2	8.5	3.71	11.4	43.1	27.4	9.0
Ca-Hardness	Average	98.5	79.3	41.6	92.2	93.7	87.4	84.8	48.9	95.0
	STDev	4.8	8.9	10.5	8.5	4.2	8.5	11.1	2.3	3.6
Mg-Hardness	Average	31.0	30.9	31.1	28.6	26.8	29.3	29.5	30.2	30.8
	STDev	6.1	6.6	5.73	3.1	4.1	4.8	5.6	4.0	7.3
NH_2Cl	Average	0.06	0.43	2.19	0	0	0	0.16	2.12	0
	STDev	0.20	0.37	0.72	0	0	0	0.18	0.64	0
NH_2Cl Dosed	Average	0.49	0.67	0.84	0	0	0	0.38	0.91	0
	STDev	0.02	0.28	0.71	0	0	0	0.15	0.62	0
Total SiO_2	Average	7.81	10.8	10.8	16.3	21.2	26.0	25.4	16.1	10.7
	STDev	0.7	0.7	0.48	0.84	0.92	0.9	0.9	0.9	1.0
Total SiO_2 dosec	Average	0	0	0	0	0	0	0	0	0
	STDev	0	0	0	0	0	0	0	0	0
Dissolved	Average	6.0	6.3	6.42	6.17	6.16	6.31	6.11	6.38	6.27
Oxygen	STDev	1.3	1.1	0.8	0.87	0.98	0.90	0.91	1.03	0.89

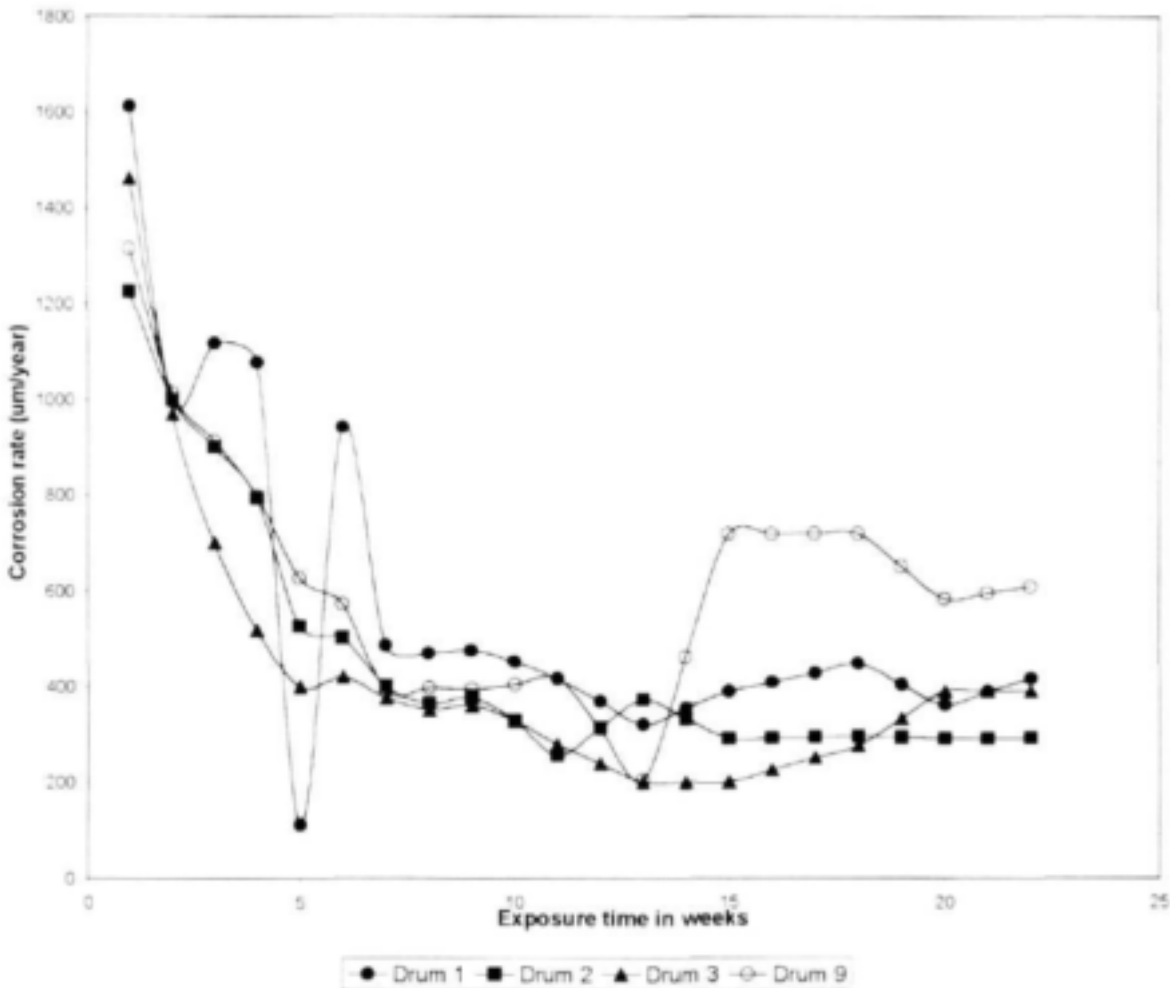
5.3 Results of the weight-loss experiment

The results of the weight-loss experiments are presented in Figures 5.1 to 5.3 for the respective treatment methods i.e. treatment with monochloramine (Figure 5.1), silicate (Figure 5.2) and a combination of monochloramine and silicate (Figure 5.3). By studying the trends of each experiment, one can make a number of observations:

- The initial corrosion rates in all tests was very high and gradually reduced to a lower limit after a period of seven weeks.
- The corrosion rates during the initial period were very erratic. The different treatments had no effect on the initial corrosion rates.
- After seven weeks equilibrium were reached in all tests.
- There is no difference in the results of tests 4, 5, 6 and the control, drum 9.
- The corrosion rates of tests 1, 2, 3, 7 and 8 were lower than the control, drum 9 or any other treatment.
- The addition of sodium silicate had no effect on the corrosion rate of the coupons.
- In all cases where monochloramine was dosed, a reduction in the corrosion rate was measured.
- Lower corrosion rates were observed at higher monochloramine dosages.

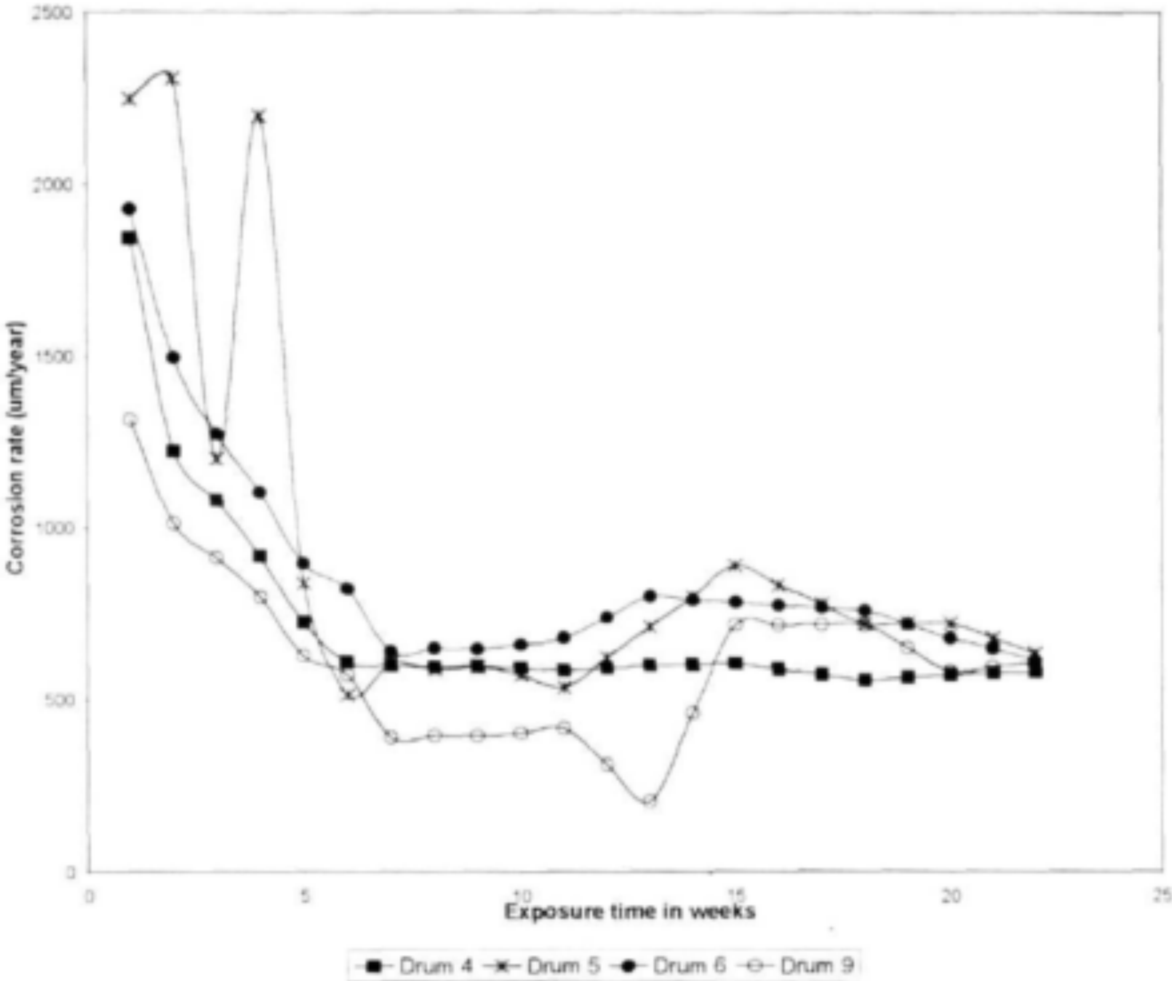
- The lowest corrosion rates were observed in drum 8 that contained a relatively high concentration of monochloramine at 3 mg/ℓ and 5 mg/ℓ of silicate. Corrosion rates in this water were comparable to that in water with only monochloramine and were lower than in water without any additives.

The results of measured corrosion rates from the seventh week onwards were analyzed and presented in Table 5.3, which clearly demonstrates the corrosion-inhibiting effect of monochloramine.



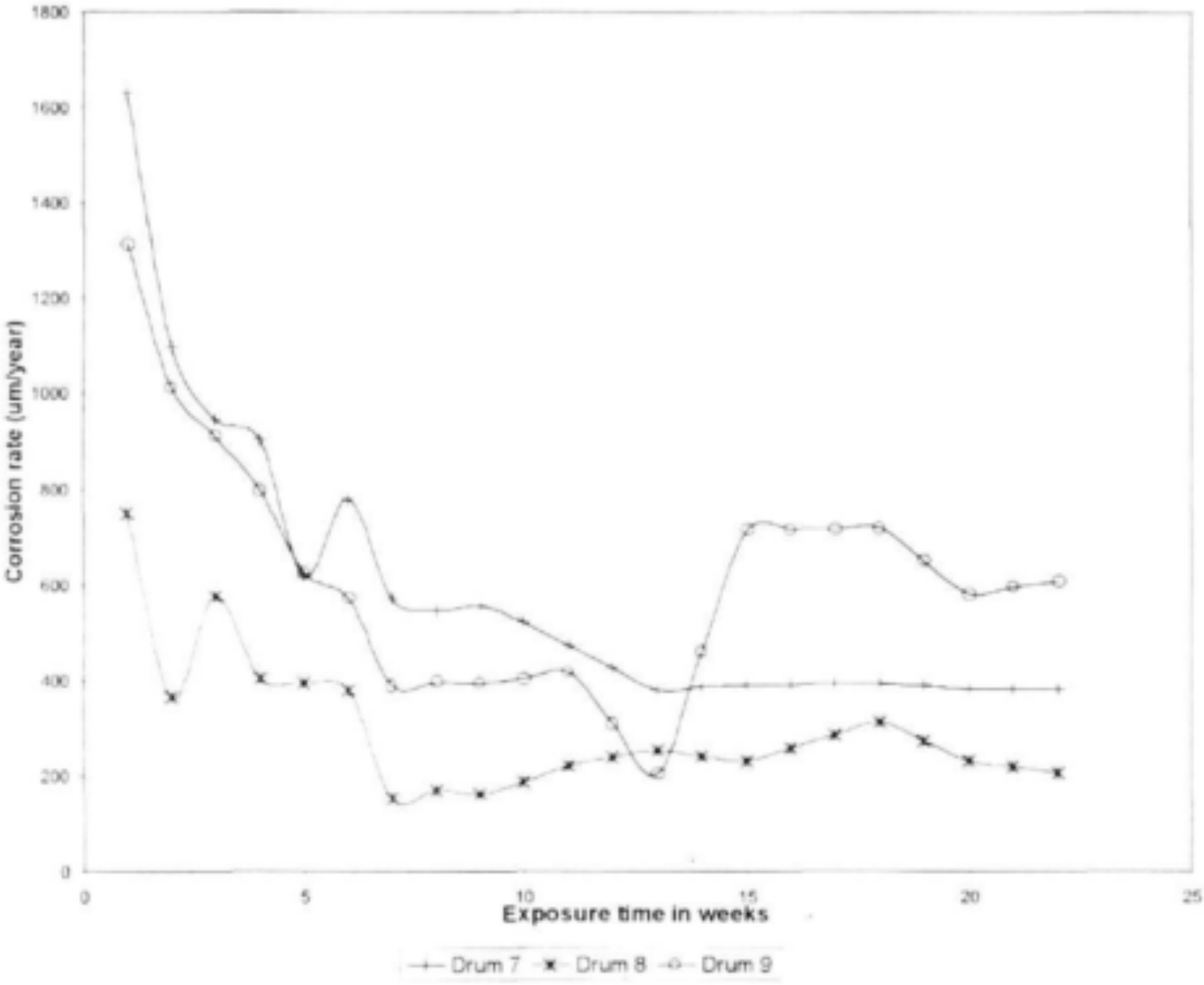
Control-Drum 9

Figure 5.1 Measured corrosion rates on pipe coupons in water containing different monochloramine concentrations compared with a control without any additives.



Control-Drum 9

Figure 5.2 Measured corrosion rates on pipe coupons in water containing different silcate concentrations compared with a control without any additives



Control-Drum 9

Figure 5.3 Measured corrosion rates on pipe coupons in water containing mixtures of monochloramine and silicate at different concentrations compared with a control without any additives

Table 5.3 Average values and standard deviation of the corrosion rate results from week 10 to week 22 during the weight-loss experiment.

		Drum 1	*Drum 2*	*Drum 3*	*Drum 4*	*Drum 5*	*Drum 6*	*Drum 7*	*Drum 8*	*Drum 9*
Corrosion rate µm/year	Average	392	301	281	583	722	730	398	248	664
	STDev	36	28	76	15	97	61	27	31	61

Drum 1 0.5 mg/ℓ monochloramine
Drum 2 1.0 mg/ℓ monochloramine
Drum 3 3.0 mg/ℓ monochloramine
Drum 4 5.0 mg/ℓ sodium silicate as SiO_2
Drum 5 10 mg/ℓ sodium silicate as SiO_2
Drum 6 15 mg/ℓ sodium silicate as SiO_2
Drum 7 0.5 mg/ℓ monochloramine + 15 mg/ℓ sodium silicate as SiO_2
Drum 8 3.0 mg/ℓ monochloramine + 5.0 mg/ℓ sodium silicate as SiO_2
Drum 9 no additives-filtered water

Samples of the corrosion products were taken from the coupons of each treatment and after digesting it in acid, analyzed with an ICP to determine its cation composition. A summary of the results is presented in Table 5.4. The SiO_2 content of coupons from drums 5 and 6 were higher than the remainder of the samples, indicating incorporation of some silica in the scale. The higher CaO content of the scale on coupons from drums 4, 7 and 8 was also reflected in the softening of the water in the different treatments.

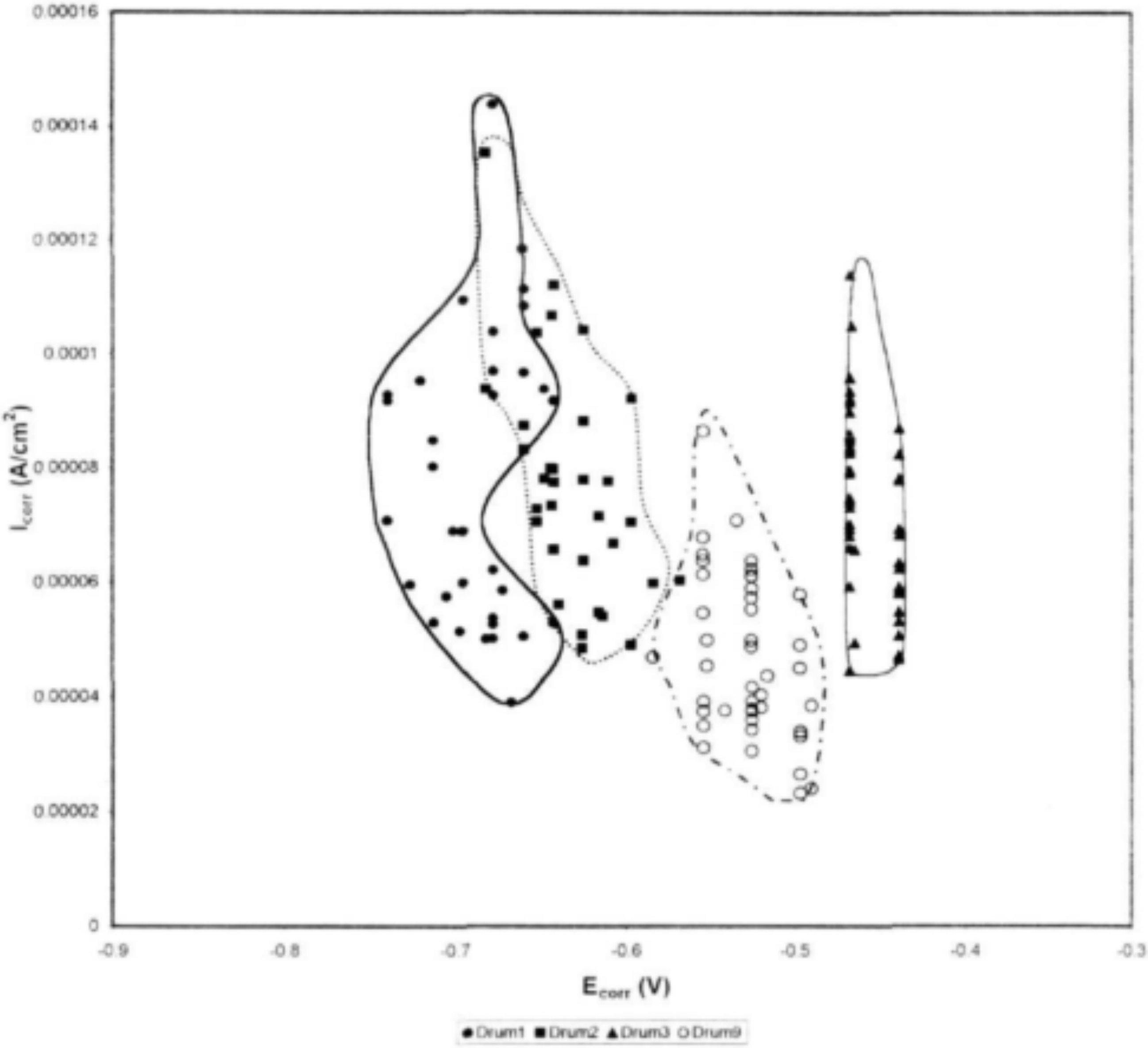
Table 5.4 Chemical analyses of the corrosion products collected from the specimens during the weight-loss experiments.

Parameter		*Drum 1*	*Drum 2*	*Drum 3*	*Drum 4*	*Drum 5*	*Drum 6*	*Drum 7*	*Drum 8*	*Drum 9*
Loss or ignition	Average	10.9	14.6	18.3	11.8	9.85	14.3	12.8	19.9	13.8
	STDev	4.3	7.7	15.8	5.5	10.8	7.8	5.5	17.5	4.9
SiO_2	Average	6.4	7.2	8.5	4.4	11.8	13.1	6.6	4.0	5.6
	STDev		9.9	12	0.25	11.6	12.7	5.42	2	5.4
Al_2O_3	Average	4.2	1.9	0.8	0.85	0.8	0.8	0.9	4.0	5.6
	STDev	3.7	3.1	0.9	1.1	1.0	1.1	1.3	2.0	5.4
Fe_2O_3	Average	81	86	84	67	83	82	73	69	93
	STDev	9.1	17.2	19.2	40.6	17.8	19.0	40.7	49	7.5
Cr_2O_3	Average	0	0	0	0	0	0	0	0	0
	STDev	0	0	0	0	0	0	0	0	0
TiO_2	Average	0.08	0.12	0.1	0.4	0.05	0.07	0.06	0.05	0.03
	STDev	0.07	0.14	0.1	0.04	0.06	0.07	0.08	0.04	0.04
CaO	Average	1.07	1.31	2.35	18.76	3.44	2.9	21.5	29.3	3.78
	STDev	0.89	1.47	2.75	27.5	2.6	2.2	34.8	47.8	0.68
MgO	Average	0.27	0.24	0.28	0.46	0.4	0.37	0.42	0.63	0.35
	STDev	0.07	0.19	0.23	0.47	0.3	0.3	0.57	0.81	0.14
K_2O	Average	0.04	0.11	0.03	0	0.09	0.11	0.04	0	0.05
	STDev	0.06	0.18	0.06	0	0.11	0.11	0.06	0	0.07
Na_2O	Average	0.01	0.04	0.03	0	0.6	0.11	0.01	0.02	0.04
	STDev	0.02	0.07	0.05	0	0.07	0.09	0.01	0.01	0.05
Zn	Average	0.33	0.23	0.08	0.07	0.08	0.07	0.38	0.03	0.05
	STDev	0.48	0.33	0.12	0.08	0.13	0.11		0.05	0.07
P_2O_5	Average	0.05	0.08	0.6	0.01	0.09	0.1	0.11	0.05	0.08
	STDev	0.07	0.12	0.09	0.01	0.11	0.13	0.15	0.04	0.1
MnO_2	Average	0.43	0.43	0.8	0.21	0.86	0.73	0.3	0.37	0.68
	STDev	0.31	0.25	0.71	0.13	0.12	0.87	0.18	0.25	0.85
C	Average	2.35	2	4.01	3.71	1.47	1.2	4.56	4.86	3.31
	STDev	2.14	2.26	5.98	4.05			6.34	6.37	3.13
S	Average	0.12	0.12	0.05	0.09	0.03	0.07	0.21	0.06	0.05
	STDev	0.05	0.09	0.02	0.03			0.09	0.05	0.02

5.4 Results of the rapid scanning technique

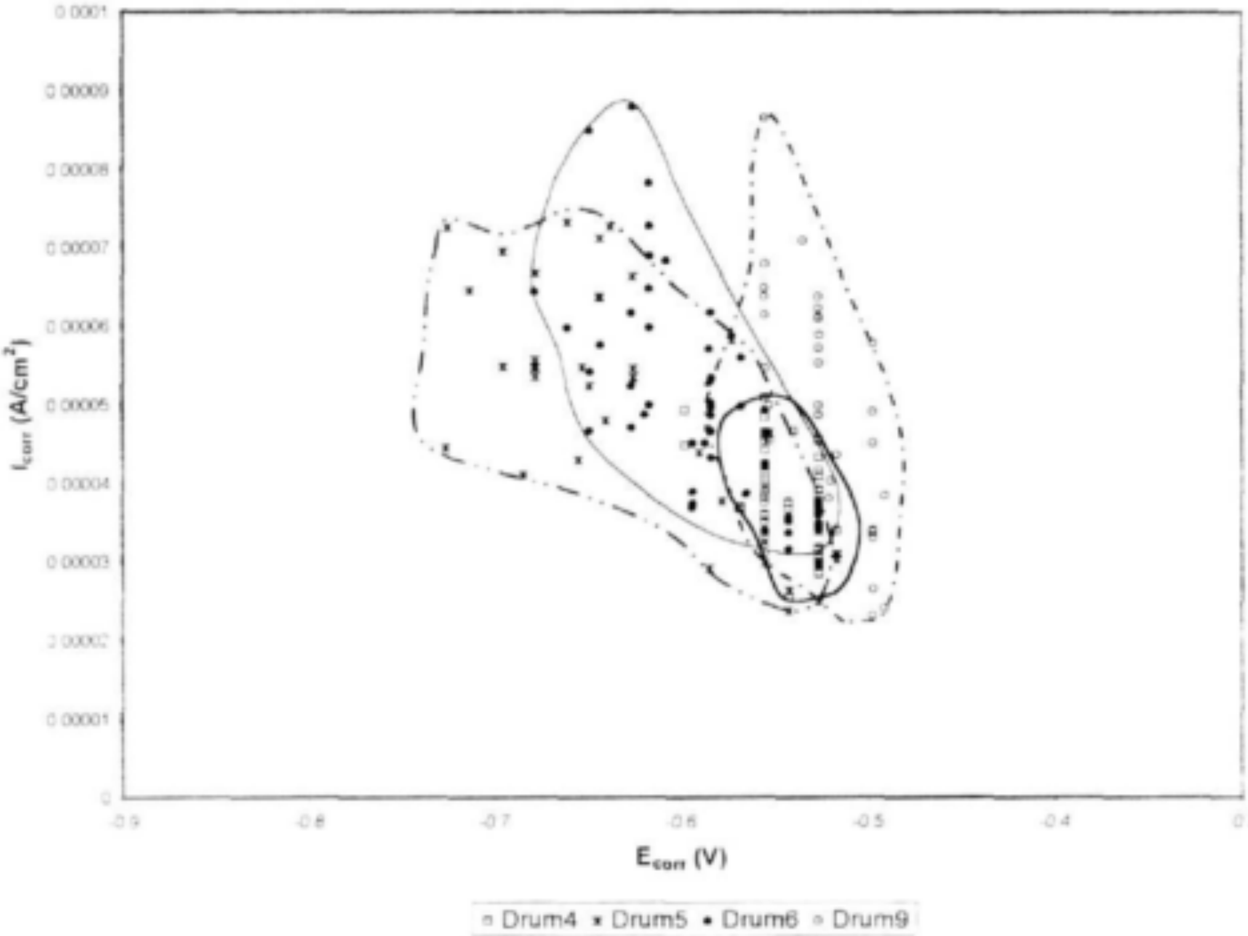
It was observed with the rapid scanning technique that equilibrium of the corrosion rate was only reached after seven weeks. After this period, a steady rate was set in. The general pattern was the same as observed with the weight-loss experiment. It was found useful to present the results in a format where the measured current was expressed in terms of the potential of the surface of each specimen measured against a standard reference electrode. The results are displayed in Figures 5.4 to 5.6 for respectively the three treatment methods that were applied while the data is summarized in Figure 5.7.

It was clearly demonstrated that the results of each treatment are grouped within certain limits of I_{corr} and the measured potential, E_{corr}. In Figure 5.7 the data points were removed and blocks were drawn for each group. The vertical boundaries of each block are respectively one standard deviation below and above the average value of the measured E_{corr} values for each treatment. The horizontal boundaries are respectively one standard deviation below and above the average applied current density. The average values for current densities and E_{corr} values were linked with a trend line.



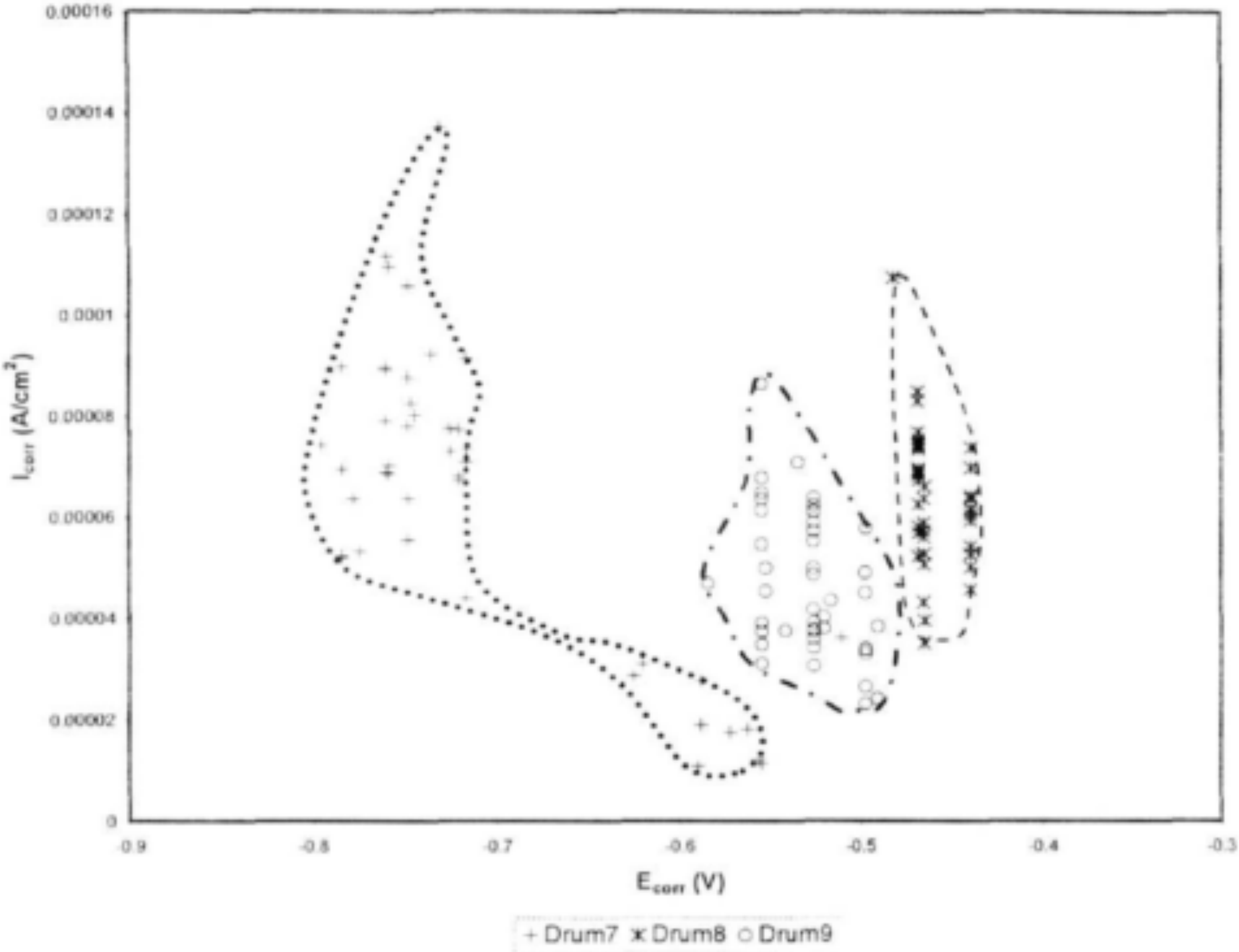
Control - Drum 9

Figure 5.4 Clustered data of measured current (I_{corr}) versus potential (E_{corr}) in rapid scanning tests in water containing different monochloramine concentrations compared with a control without any additives.



Control – Drum 9

Figure 5.5 Clustered data of measured current (I_{corr}) versus potential (E_{corr}) in rapid scanning tests in water containing different silicate concentrations compared with a control without any additives.



Control - Drum 9

Figure 5.6 Clustered data of measured current (I_{corr}) versus potential (E_{corr}) in rapid scanning tests in water containing mixtures of monochloramine and silicate at different concentrations compared with a control without any additives.

The following observations are derived from Figure 5.7:

- Data from drums 4, 5 and 6 is closely scattered in the middle with the lowest I_{corr} values. It implies that the corrosion rate of the control and the treatment with only sodium silicate were lower than the other treatments.
- The current density of the samples treated with only monochloramine were higher, but the surface potential of these treatments were either below or above that of the treatments without monochloramine.
- Where sodium silicate and monochloramine were dosed simultaneously, the results were similar to the results obtained with only monochloramine. Drums 1 and 7 gave similar results and so did drums 3 and 8.

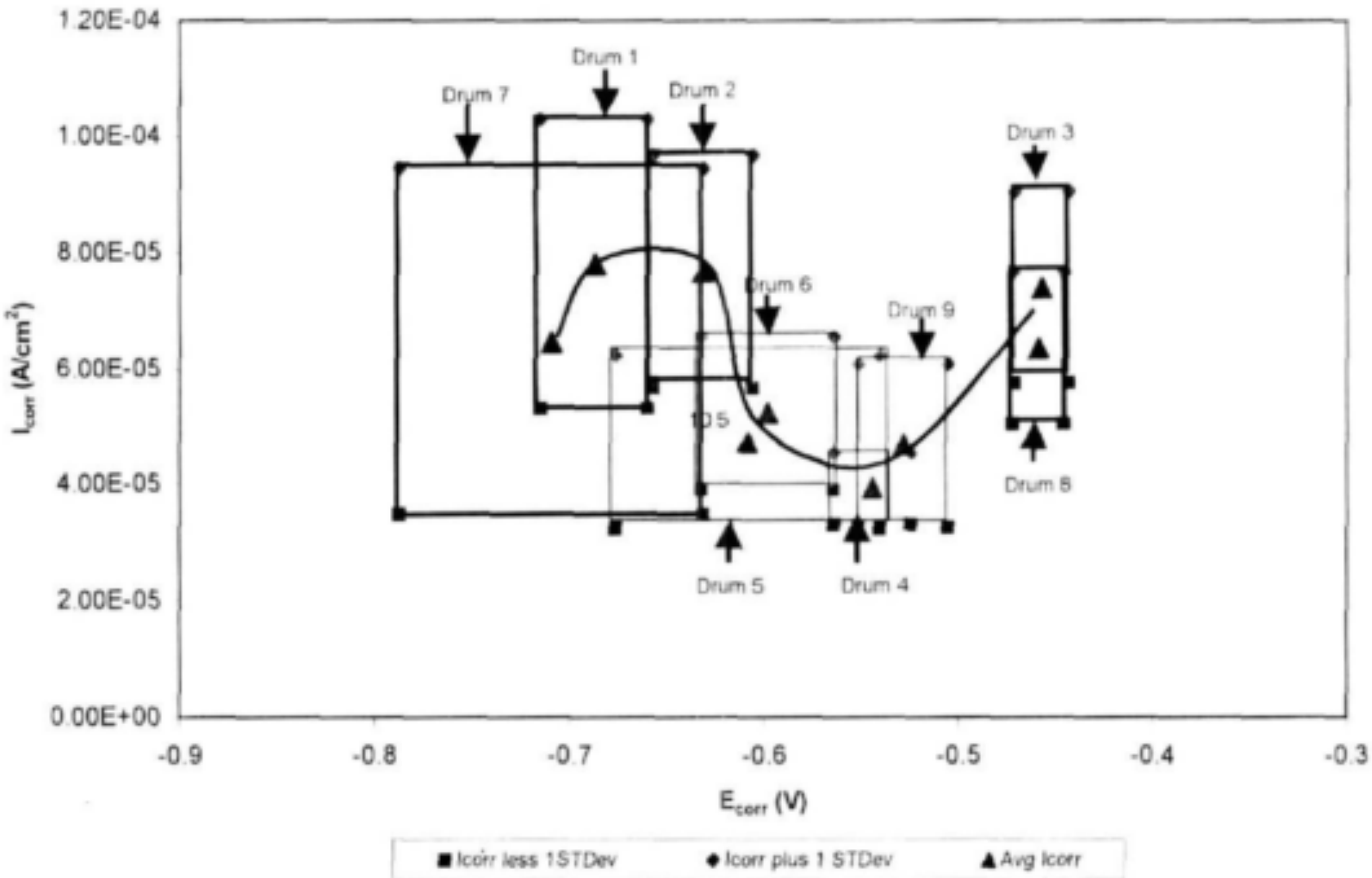


Figure 5.7 I_{corr} and E_{corr} values from rapid scanning tests representing different treatments grouped within 1 standard deviation below and above the average values and shown with a trend line.

CHAPTER 6

6. DISCUSSION AND CONCLUSIONS

The results show clearly that the corrosion rates initially are very high and do not reflect the method of treatment. This implies that no attempt should be made to measure the long-term effect of an inhibitor used in potable water during the first few weeks of exposure. The minimum time before equilibrium was reached for the experiments described in this document, was seven weeks.

In the weight-loss experiments, lower corrosion rates were measured with the addition of monochloramine, even when it was dosed in combination with sodium silicate. Lower corrosion rates were measured with incremental higher dosages.

The addition of only sodium silicate had no effect on the measured corrosion rate as compared with the control sample without any additives. Although the analysis of the corrosion products indicated the presence of silicate, it can be concluded that it had no effect on the corrosion rate. However, there is overwhelming evidence in the literature that support the claim that sodium silicate is an effective corrosion-inhibitor. It is possible that the duration of the experiments was not long enough to observe its effect since sodium silicate is only effective when the tertiary corrosion products are formed.

The rapid scanning technique demonstrated completely different results. The I_{corr} values with the monochloramine treatments demonstrated higher corrosion rates compared with the control and the treatments with only sodium silicate. An analysis of the data, where the I_{corr} values are plotted in relation with the E_{corr} values, demonstrates that there is a narrow region of E_{corr} values where corrosion is limited. At a surface potential below or above these values, increased corrosion rates are measured. The results clearly show that, at higher monochloramine concentrations, higher corrosion rates are measured. At lower dosages, corrosion was also stimulated.

It appears then that there is a narrow margin within which the monochloramine concentration should be maintained to protect the mild steel pipelines. It also appears that it is in the same level of 1-2 mg/ℓ as required for bacteriostatic activity.

This has a significant practical implication since monochloramine can be used to passivate the surface of corroding metal, provided that concentrations are controlled within the required limits.

It is recommended that in order to optimise the use of monochloramine field tests should be conducted at several points in a distribution network in order to find a correlation between the surface potential of the pipeline, the monochloramine concentration in the bulk of the water, the bacteriological quality of the water and the corrosion rate.

CHAPTER 7

7. RECOMMENTATION FOR FUTURE RESEARCH

- Conduct a study into the mechanism of corrosion inhibition by monochloramine and silicate.

- Investigate the application of monochloramine and silicate as corrosion inhibitors in water with chemical composition typical to the soft coastal water compared to harder inland water.

- Investigate the use of monochloramine and silicate as corrosion inhibitors for other metals than mild steel, such as copper tubing.

CHAPTER 8

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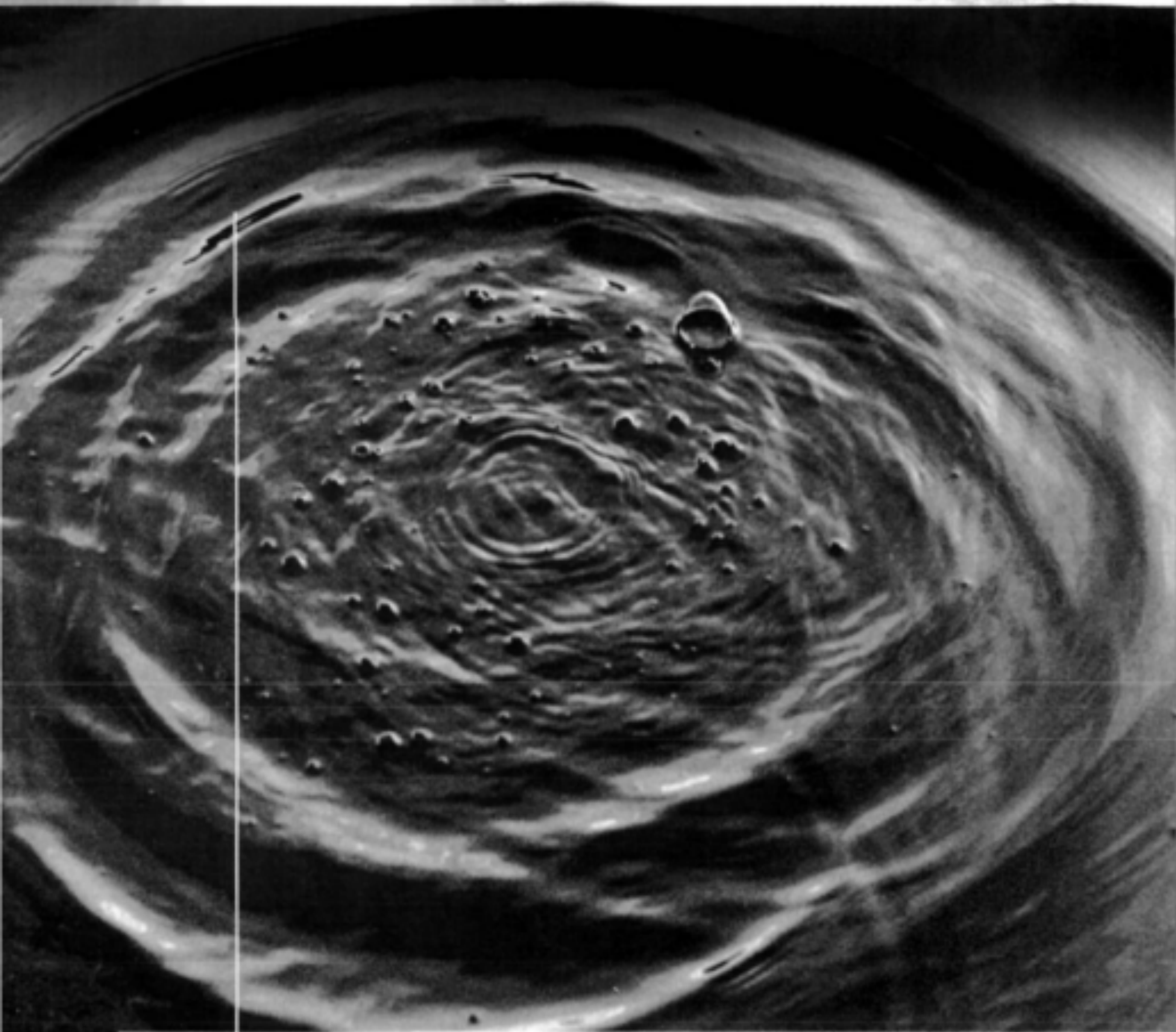

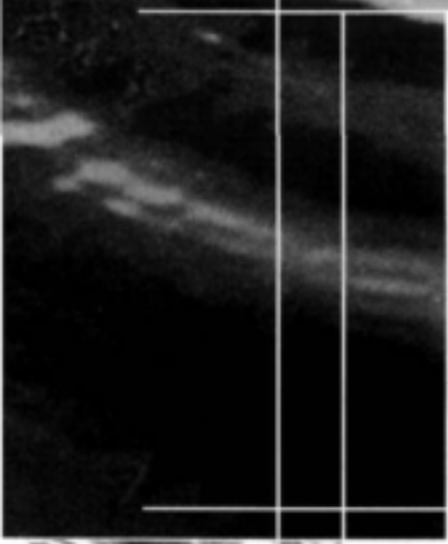

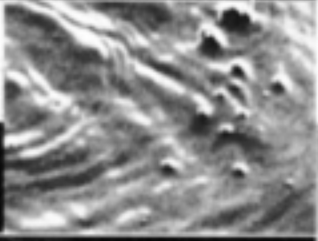

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