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LICENTIATE THESIS

Iron Corrsion in Drinking Water Distribution Systems - A Corrosion Rate Study

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Nothing in the world is more important than water,
because without it nothing can come to life
or continue to exist.

Ingenting i världen är viktigare än vatten,
för utan det kan intet komma till liv
eller fortsätta existera.

(Marcus Pollio Vitruvius, ca 40 f. Kr.)

Preface

Corrosion comes from the Latin word 'corrodere' which means 'gnaw to pieces'. The definition of corrosion is 'the deterioration of a substance or its properties because of a physical-chemical reaction with its environment', Schock (1990).

Internal corrosion of drinking water pipes is the biggest quality problem within the field of water distribution. Several different pipe materials are used and iron is the most common material in. Iron reacts with oxygen in the water and causes deterioration of pipe and water quality. Failure of the pipe itself will cause leakage and loss of hydraulic capacity. The result of transporting water through a corroding network is an increase in concentrations of metals like iron, copper, zinc and, depending on the pipe materials, lead in the water. Microorganisms usually grow in deposits of corrosion products. These processes can cause water quality problems such as red colour, taste, odour and bacteria. Heavy metals in the water will end up in the sludge from the sewage treatment plants and make it less valuable as a fertilizer.

This licentiate thesis is part of a project in Sweden called "The influence of Water Quality on Corrosion of Iron and Copper Pipe Materials" (Vattenkvalitetens betydelse för korrosion på dricksvattenledningar av järn och koppar) - a program including kinetic studies, pilot scale studies and applied investigations in Swedish cities. The Department of Sanitary Engineering at Chalmers University of Technology is responsible for coordinating the project and carrying out the research in cooperation with the Department of Inorganic Chemistry at Gothenburg University.

The Swedish Water and Waste Water Works Association, VAV, has financed this project during a four year period, finishing in 1996. Fifteen municipalities have contributed to the project in the applied investigations and the pilot scale studies. The financial support from VAV and communities is gratefully acknowledged.

I would like to express my gratitude to my supervisors Torsten Hedberg and Bo Berghult for their enthusiasm, guidance and support, for sharing their knowledge and ideas from a long experience within this field and for giving me valuable comments on the thesis.

I would like to thank Greg Morrison for linguistic help and advice, and valuable comments.

I would also like to thank Ann Elfström Broo and Eva Lind Johansson (also working within this project), all of my colleagues at the Department of Sanitary Engineering and Elisabet Ahlberg at the Department of Inorganic Chemistry. They have all been good friends and contributed to a stimulating and enjoyable research environment, in both practical and more visionary aspects.

Finally, I want to thank Pelle, my husband, for all his support and understanding.

Göteborg 11 November 1996

Abstract

Corrosion in drinking water systems is a world wide problem. Until now, water utilities have had limited knowledge to predict what water treatments are necessary to reduce iron corrosion problems. Instead “trial and error” have often been used for each case. Understanding the mechanism for corrosion coupled to different water quality parameters would make better predictions possible. There is considerable evidence that pH-value, calcium and hydrogen carbonate content are important factors. The impacts of these factors have been studied in the laboratory and compared with a field investigation in several municipalities in Sweden. An electrochemical method, potentiodynamic sweeping, and coupon tests were used to determine the corrosion rate of iron.

The corrosion rate correlates to the logarithm of the free carbon dioxide (the sum of protonated carbonic acid and dissolved carbon dioxide) content. In low alkalinity waters the addition of calcium decreases the initial corrosion rate. At higher alkalinity no distinct dependence on calcium concentration is observed. These observations are in accordance with observations made in the field investigation and in other countries.

As a possible explanation for the iron corrosion dependence on the carbonate system and calcium content, a surface complexation model is proposed. In the presence of free carbon dioxide, surface complexes of iron-hydrogen-carbonate or iron-carbonate form. If the total carbonate content is low and calcium added, surface complexes such as iron-oxygen-calcium form. At higher total carbonate and calcium concentrations the complexes involving hydrogen carbonate or carbonate will dominate over the ones involving calcium.

This theory was further investigated with calculations on surface reactions. The surface complexation properties of the system have been correlated with experimental data and field investigation data. Surface complexation seems to be a relevant model to explain the iron corrosion dependence on drinking water quality. How the initial corrosion rate and the release rate from corrosion products depend on different surface complexes have been suggested, but not the exact mechanisms behind iron corrosion.

Keywords: iron corrosion, drinking water, carbonic acid, free carbon dioxide, calcium, surface complexation

Sammanfattning

Korrosion i dricksvattensystem medför problem överallt i världen. Vattendistributörerna har hittills fått prova sig fram till vilka förändringar av olika vattenkvaliteter som krävs för att minimera korrosionsproblemen. Ökad kännedom om olika vattenkvalitetsparametrars inverkan på mekanismen bakom korrosionsreaktionerna skulle medföra att den bästa behandlingsmetoden för ett visst vatten kan förutses. Litteraturstudien visar att korrosion i järnledningar i hög grad påverkas av vattnets pH-värde, kalcium- och vätekarbonathalt.

Effekten av pH-värde och koncentrationen av vätekarbonat och kalcium på korrosion av järn har studerats med olika metoder i laboratorieskala. Dessa resultat har jämförts med resultaten från en fältundersökning i ett 15-tal kommuner i Sverige. För att bestämma korrosionshastigheten användes en elektrokemisk metod, potentiodynamiska svep, och kupongtester.

Korrosionhastigheten för järn korrelerar till logaritmen av halten fri kolsyra i vattnet. Tillsats av kalcium till ett vatten med låg alkalinitet medför att den initiala korrosionhastigheten hos järn sjunker. Vid högre alkalinitet observerades ingen tydlig påverkan på korrosionshastigheten. Fältundersökningen och studier i andra länder med varierande vattenkvaliteter uppvisar liknande observationer.

För att förklara järnkorrosionens beroende av karbonatsystemet och kalciumhalten i vattnet föreslås en ytkomplexmodell. Fri kolsyra i vattnet medför att ytkomplex av järn-vätekarbonat eller järn-karbonat bildas. Vid låga totalhalter av karbonat medför en kalciumtillsats att ytkomplex som till exempel järn-syre-kalcium bildas. Vid högre totalhalt karbonat och högre kalciumhalt dominerar ytkomplexen med karbonat eller vätekarbonat över dem med kalcium.

Modellen testades och vidareutvecklades med hjälp av beräkningar på ytreaktioner. Systemets beräknade egenskaper vad gäller bildning av ytkomplex jämfördes med experimentella data och fältmätnings data. Ytkomplex förefaller vara en bra och relevant modell för att förklara vattenkvalitetens inflytande på järnkorrosion. Den exakta mekanismen bakom järnkorrosion i dricksvatten har inte kunnat bestämmas. Däremot lämnas ett förslag till mekanismen för hur den initiala korrosionhastigheten och utlösningshastigheten av korrosionsprodukter beror på olika ytkomplex.

Contents

1. Introduction

1.1. The corrosion problem and the consequences of corrosion

People in different parts of the world are starting to realise that if mankind is to survive we should build a sustainable society, Robért (1992) and Holmberg (1995). This means sustainable relationships between the global society and the ecosphere and also within the society itself. How we take care of the water on the globe is an important part of a sustainable society. We need water for many purposes and we need drinking water with good quality. Therefore we cannot allow continuous contamination of the ground or the water resources and we need an effective way of recycling water.

Communities world wide are investing large amounts of money in environmental technology to improve sustainability. The municipal sector takes up a considerable share of that sum, and distribution systems for drinking water and wastewater account for 80% of the investments in this sector. For drinking water systems in Sweden, 4 500 million SEK (590 SEK/person) have been invested in operation and maintenance and 442 million SEK (58 SEK/person) in new pipes during 1994 (renewal time 240 years), VAV - Swedish Water and Wastewater Works Association (1995) (1 SEK = 0.15 US $, Aug. 1996).

Many factors affect operation and maintenance costs and the lifetime of pipes. External corrosion is regarded as one major factor, Mattsson (1992), as it causes pipe breaks and overflows. Internal corrosion is usually not decisive for the lifetime of municipal pipes, but may be so for private plumbing systems. The major effect of internal corrosion of municipal pipes is deterioration of the water quality delivered to consumer taps, for example, bad taste and red water. Internal corrosion often causes deposition of corrosion products as a scale on the pipe wall. This scale reduces the effective diameter of the pipe and therefore pumping costs will increase. Microorganisms can find a good environment for regrowth in the scale, Hack (1986), and then cause bad taste and odour. To minimize these problems not only the corrosion of the pipe is to be considered, but also formation and dissolution of corrosion products.

Heavy metals originating from corrosion both in drinking water and wastewater systems will be found in the sludge from sewage treatment plants, which will then be less valuable as a fertilizer. Seen in a longer perspective it is also a waste of valuable metals from finite sources since recycling the metals is very difficult, or impossible, after they have been diluted in the recipient of the sewage treatment plant, dumped on a waste site as sludge or spread over farmlands. Therefore, the challenge for the future is to minimize corrosion products dissolved in drinking water and wastewater and concentrated in sewage sludge.

As a consequence of the expenses for water and sewage networks and of the necessity to recycle the sludge from sewage treatment plants, the interest in corrosion control in drinking water systems is increasing. A question that remains to be answered is whether changing the water quality or the pipe material is the solution to avoid corrosion problems. This has intensified the need for studies of the influence of water quality on the corrosion rate in water pipes. Several studies have shown that to reduce corrosion various pipe materials require various water qualities, Sontheimer *et al.* (1985), Kuch (1985), Snoeyink and Kuch (1985), Lind Johansson (1989) and, Vik and Hedberg (1990). This means that if we want to minimize corrosion in the future, some materials should be excluded from use in the distribution systems.

Water parameters such as the total concentration of carbonate (carbonic acid, hydrogen carbonate and carbonate), content of calcium ions, organic matter, chloride and sulphate ions, pH and temperature, all influence the corrosion process in different ways. Good corrosion prevention methods require a specific understanding of how the different water parameters interact with different pipe materials. Changing the concentrations of the carbonate system components, the calcium content and the pH-value are relatively easy and frequently used treatment methods at the water works. Today the adjustments are often modified based on experience. With a deeper knowledge about corrosion mechanisms corrosion prevention methods can become more efficient and less costly.

Addition of corrosion inhibitors to drinking water as a way of solving the corrosion problems is not consistent with a sustainable society. Therefore it is likely that minimizing the corrosion problem in the future will be realized by other adjustments of the water quality and a direction towards more homogeneous pipe materials.

Hedberg *et al.* (1995) conclude that to avoid corrosion problems, our water networks should consist of only one pipe material, or materials that require the same or almost the same water quality. In several countries the guidelines recommend a relatively high pH-value for drinking water, up to between 8 and 9 is common. In Sweden the guidelines recommend the pH-value to be between 7.5-9.0, SLV - Swedish National Food Administration (1993). This is mainly because copper pipes corrode less at high pH-values. If the guidelines only have to consider different iron materials the recommendations for pH may be lower (maybe around 7), as can be seen from this literature review.

The details of the relationship between pipe material and the chemical composition of the water are not well understood. Many investigations describe specific networks and their corrosion problems and how different treatment methods improve the quality of the distributed water, Committee on Control of Water Quality in Transmission and Distribution Systems (1984), Reiber *et al.* (1987), Pisigan and Singley (1987), Enander and Berghult (1994). Since water composition is very complex and differs from place to place, detailed investigations with well-controlled water composition and one pipe material at a time are necessary to allow an understanding of the chemistry and the mechanisms that cause corrosion.

The conditions in the pipes are continuously changing and the corrosion processes are too slow to reach equilibrium. For that reason measuring the content of different corrosion products is not enough to be able to predict the corrosion rate. Instead we need to understand how the reactions behind the corrosion proceed. To achieve this understanding electrochemical methods are suitable since they give information about the reaction rates and of the mechanisms for the reactions under controlled circumstances.

1.2. Objectives

The principal objectives of the project "The influence of Water Quality on Corrosion of Iron and Copper Pipe Materials" are to improve the understanding of how water quality affects corrosion in drinking water pipes of iron and copper and to find the optimal water quality to minimize corrosion problems.

This thesis is a part of the project. It aims to find out the influence of the different components of the carbonate system and the calcium concentration on the corrosion rate of iron in slightly alkaline solutions, such as drinking water with pH-values between seven and nine.

1.3. Scope of the investigation

The project is divided into four different parts. Part one is the basis for this licentiate work.

1. Laboratory measurements using scientific electrochemical techniques to study the corrosion mechanisms.
2. Pilot plant studies using ordinary piping and a wide range of water qualities.
3. Collection and analysis of water samples from the municipalities, including speciation of different corrosion products.
4. Full scale tests.

This licentiate thesis summarizes the results from laboratory investigations and some field investigations concerning corrosion on iron, presented in two articles, Appendix 1 and 2, Sander *et al.* (1996 a), Sander *et al.* (1996 b). The laboratory work included electrochemical experiments and coupon tests with iron in synthetic drinking water, that is distilled water with different additions of hydrogen carbonate and calcium.

2. Corrosion of iron pipes - literature review

2.1. *Corrosion of iron pipes*

When iron corrodes, metallic iron is dissolved and iron(II) ions are formed, Gellings (1985) and Schock (1990). The driving force behind the corrosion process is the difference in potential that evolves on a metal surface due to inhomogeneous materials, contact with another metal, deposited corrosion products, varying flow velocity and microbiological processes. Metal dissolution is an electrochemical reaction and consists of two partial reactions, one anode and one cathode-reaction. Positively charged iron(II) ions form during oxidation at the anode. The electrons produced at the anode will be consumed during reduction at the cathode. In drinking water pipes the reduction is usually oxygen reduced to hydroxide.

anode: $Fe \longrightarrow Fe^{2+} + 2\,e^-$ (1.1)

cathode: $\frac{1}{2}\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^-$ (1.2)

The corrosion rate, the rate with which a metal dissolves, and other electrochemical reactions are dependent on the rate of:

- the transport of dissolved reactants, here oxygen, to the metal surface
- the electron transfer from anode to cathode
- the transport of corrosion products from the surface to the bulk liquid according to for example Snoeyink and Kuch (1985), Schock (1990) and Southampton Electrochemistry Group (1990).

The corrosion of iron in acidic solutions means active corrosion and dissolution of the metal. It is well known and described by several authors, for example Nilsson (1979), Håkansson (1982), Ström (1988) and Friel (1989). Iron corrosion in alkaline solutions, like drinking water, is complex since it includes the formation and dissolution of a passive layer of different corrosion products. The iron(II)ions from the dissolution of the metal react further with for example hydroxide, oxygen, carbonate or hydrogen carbonate present in the water. These corrosion products can form either protective, dense scales, well connected to the wall, porous, unprotective scales and/or products carried by the water. The two latter ones cause increasing corrosion problems instead of protection.

In the drinking water field distinguishing between uniform corrosion, pitting corrosion and corrosion related water quality problems are important.

- *Uniform corrosion* is a process where the metal loss is relatively uniform over the surface. Uniform corrosion causes formation of corrosion products, both products forming scales on the inside of the pipe and products transported with the water.
- *Pitting corrosion* is a process where the metal loss is concentrated to limited spots on the surface and forms pits or holes in the pipe wall.
- *Corrosion related water quality problems*, which are those most commonly experienced by consumers, are mainly a function of the precipitation and dissolution of the corrosion products formed, Kuch and Sontheimer (1986) and Kuch (1988).

This literature review concentrates on uniform corrosion and corrosion related water quality problems.

2.2. *Corrosion studies*

The objectives for a corrosion study can be many, for example, Kuch (1985):

- determine the corrosiveness of one water supply relative to others;
- determine the concentrations of corrosion products;
- determine the corrosion rate and cause of pitting corrosion;
- determine the effectiveness of corrosion control measures;
- conduct basic studies to determine the mechanisms of corrosion.

Depending of the objectives, different techniques are used. Corrosion monitoring methods include weight loss techniques, physical inspection of corroded surfaces and electrochemical methods. Weight loss techniques, with removable coupons or pipe parts inserted in pipe loops or in plumbing systems, are widely used in field investigations for different municipalities. Supplementary information can be obtained by physical inspection of pipe surfaces and corrosion products, either visually or by different types of spectroscopy, microscopy or x-ray diffraction. Different techniques used in corrosion studies of iron are described in Singley and Lee (1984), Committee on Control of Water Quality in Transmission and Distribution Systems (1984), Kuch (1985), Schock (1990), Ferguson *et al.* (1995) and Hedberg *et al. (1995).*

2.3. *Parameters influencing iron corrosion*

The corrosion processes are influenced by chemical, physical, biological and metallurgical factors, Larson and Skold (1957), Snoeyink and Kuch (1985), Schock (1990) and Mattsson (1992). Examples of influencing factors are temperature, flow velocity, pipe material, microbiological activity and different water quality parameters, such as pH-value, buffer capacity, hardness, content of carbonic acid, hydrogen carbonate, carbonate, chloride, sulphate and organic matter. At the water treatment plants some of the parameters, like the pH-value, the content of total carbonate and calcium, can be adjusted and sometimes corrosion inhibitors are added to minimize corrosion problems. Other parameters are difficult, or impossible, to influence. Whether the parameter can be adjusted or not, understanding its effect on corrosion is important. All the parameters interact and separating the effect of one parameter from another completely, is almost impossible.

2.3.1. Pipe materials

In Sweden 55% of the existing municipal water distribution mains are cast iron, 19% are polyvinyl chloride (PVC), 14% are polyethylene (PEH) and the rest are of a range of other materials, for example steel and stainless steel, VAV - Swedish Water and Wastewater Works Association (1995). Newly laid pipes are mainly PEH, 61%, and PVC, 25%. The total length of the municipal water mains is 66 700 km (8.8 m/connected person) plus service pipes and domestic plumbing installations. Private plumbing systems in Sweden consist almost exclusively of copper pipes and about 50% of the service pipes to houses are copper pipes. Plastic materials and stainless steel have been introduced also for private plumbing systems and service pipes.

The difference in corrosion behaviour between cast iron, ductile iron and steel is due to different chemical composition. Steel consists of more than 99% iron by weight. Cast and ductile iron are 92-93% iron and approximately 3.6% carbon and 2.5% silicon by weight, Singley and Montgomery (1985). Graphitic carbon and silicon have lower specific density than iron, which means that the difference is much larger in volume percentage. Impurities in steel are 1.1% by volume, in cast and ductile iron the volume percentage is 17-18.5. Accordingly, 15 times more surface area is occupied by nonferrous species in cast and ductile iron as in steel. This, of course, has an influence on the surface reactions. Since the surface reactions are a determining factor for corrosion, the corrosion properties of the different materials vary, Singley and Montgomery (1985).

2.3.2. The carbonate system, the calcium content and the pH-value

More than a hundred years ago Heyer (1888) (in Sontheimer *et al.* (1981)) described how drinking water was treated to limit corrosion. At that time lead pipes caused problems in Germany. Calcium was added to the water to make calcium carbonate precipitate and form a protective scale on the pipe walls.

Saturation for calcium carbonate can be achieved by increasing the pH-value or the alkalinity, Schock (1990). Alkalinity is a measure of the capacity to neutralize hydrogen ions and is defined as follows, Stumm and Morgan (1981):

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + C_x \quad \text{unit: mmol/l}$$

Hydrogen carbonate, HCO_3^-, contributes to most of this capacity in drinking water and therefore using the concentration of HCO_3^-, mg/l or mmol/l, for alkalinity is common. Distinguishing between hydrogen carbonate and alkalinity at high pH-values is important since the contribution of carbonate and hydroxide ions to alkalinity will then be significant, Stumm and Morgan (1981). C_x stands for other protolytes, such as the borate, phosphate or silicate systems or organic acids, that may be present in water. They are normally negligible in drinking water.

Hardness of water is the total content of alkaline earth metal ions. Raw waters from different areas have different hardness depending on the mineral composition of the ground. In drinking water the relevant ions are calcium and magnesium. Calcium is normally the dominant ion and therefore the units used are mg/l Ca^{2+}, mM Ca^{2+} or mg/l $CaCO_3$. Various classification systems of water containing calcium occur in various countries. The terms "hard" and "soft" water are used differently and when reading literature from different countries attention should be paid to what levels of calcium concentration are behind the used terms. The classification system presented here is used in the Nordic countries, SKTF (1953):

Table 1.1 Classification system for hardness in drinking water, SKTF (1953).

	mg/l Ca^{2+}	mM Ca^{2+}	mg/l $CaCO_3$	°d, dH
very soft water	0-14	0-0.35	0-35	0-2
soft water	14-36	0.35-0.90	35-90	2-5
medium hard water	36-72	0.90-1.80	90-180	5-10
hard water	72-145	1.80-3.62	180-350	10-20
very hard water	>145	>3.62	>350	>20

The buffer capacity, β, is closely related to the alkalinity, and the pH-value, of a water. The buffer capacity is the ability of a water to withstand pH-changes. The highest buffer capacities for the carbonate system are at the pH-values around the first and second acidity constants, pK_{a1} and pK_{a2}, that is pH 6.3 and pH 10.3 respectively, Figure 2.1. Between those, at pH 8.3, the buffer capacity has a minimum. Sontheimer (1988) suggests that the buffer capacity is the main feature of the hydrogen carbonate ions' influence on corrosion. The effect of a high buffer capacity is slow oxide formation resulting in stable corrosion products well connected to the pipe, therefore inhibiting further corrosion.

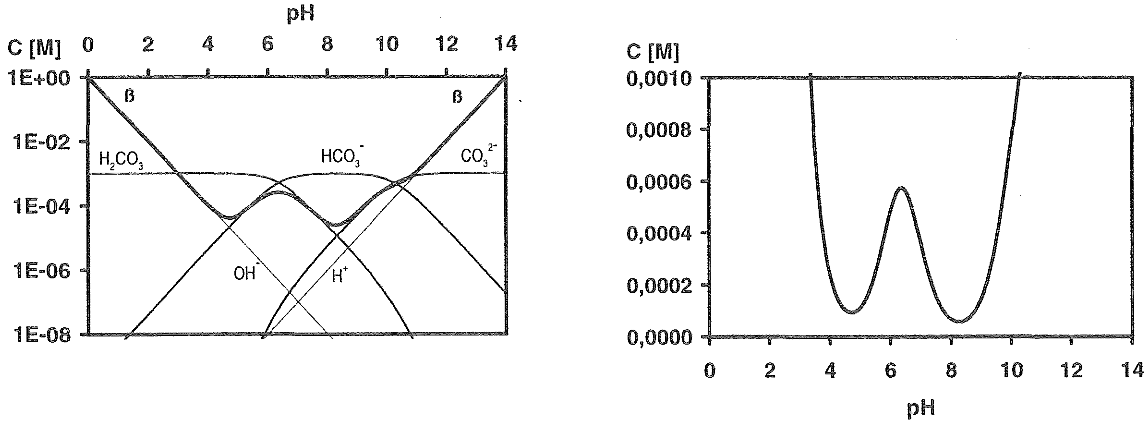

Figure 2.1 Buffercapacity as a function of the pH-value.

According to Larson and Skold (1957) corrosion products form an even scale at pH-values around 6.8, where the buffer capacity and carbonic acid content are relatively high. If the pH increases next to the pipe wall, more tuberculation occurs. Lind Johansson (1989) shows that the corrosion rate is lower when the pH-value is around 7.5 or above 9 compared with when it is 8.5, in waters with 100 mg/l calcium. At pH around 8.5 the buffer capacity is at its minimum and the hydroxide ions produced at the surface give locally a high pH. Iron then precipitates as nonprotective iron(III) products (iron(III)hydroxides, amorphous goethite and/or lepidocrocoite).

Ferguson (1985) summarizes iron corrosion in low alkalinity waters (3-15 mg/l HCO_3^-) and in waters with low hardness (<10 mg/l Ca^{2+}). These water qualities are common in several parts of the world, for example in North America and in the Nordic countries. The formation of protective films in such areas is incompletely understood. Low alkalinity waters have low buffer capacity and therefore easily affected by water treatment. Dosing of aluminium sulphate and chlorine for example, reduce the alkalinity and increase the neutral salt content. Problems with red water are common and to reduce these problems, water utilities either increase alkalinity and pH, alter treatment methods or dosages, add corrosion inhibitors (common in USA) or change the pipe materials.

Low pH-values (≤6.5) enhance uniform corrosion since the solubility of iron and the corrosion products increase and since no or very little buffer capacity is present in such waters, Ferguson (1985). High hydrogen ion concentrations also lead to an increase in corrosion rate since the ions can act as electron acceptors at the cathode. The difference in hydroxide ion concentration between the water and the corroding surface increase at low pH-values. This means that the transport rate of hydroxide ions from the surface to the bulk liquid increases and the conditions for formation of protective scales deteriorate.

The passivation of steel is promoted by a low degree of hardness and a high carbonic acid content together according to Uusitalo and Heinanen (1962). A high degree of hardness and a low carbonic acid content, on the other hand, promote the formation of a protective layer on steel composed of calcium carbonate and iron oxides. Stumm (1960) and Pisigan and Singley (1987) found that the corrosion rate decreased with increasing buffer capacity, adjusted by changing the pH-values between 6-8.5. In this pH-interval the buffer capacity covaries with the carbonic acid content.

2.3.3. Chloride, sulphate and fluoride

Elevated concentrations of chloride, sulphate and fluoride all contribute to increasing corrosion, especially pitting corrosion, and iron uptake, Larson and Skold (1957), Sontheimer *et al.* (1981), Wagner and Kuch (1984) and Kuch (1985). These anions adsorb to the corroding surface and interfere with the formation of passivating layers, Larson and Skold (1957). Hydrogen carbonate can reduce this effect. Larson recommended that the ratio $(2[SO_4^{2-}] + [Cl^-]) / [HCO_3^-]$ [mol/l] should be less than 1. Later, Hedberg *et al.* (1990) in a corrosion workshop recommended the ratio $[HCO_3^-]/(2[SO_4^{2-}] + [Cl^-])$ [mol/l] to be kept higher than 1.5 to avoid corrosion in pipes of steel, cast and ductile iron. This recommendation was based on the drinking water guidelines in several countries.

2.3.4. Chlorine

Chlorine and its reaction products cause corrosion damage to metals, Larson (1966), Pisigan and Singley (1987). Chlorine is a strong oxidizing agent. It increases the redox potential that favours conversion of iron to ferrous and then ferric ions, Singley and Montgomery (1985). Drinking water is treated with chlorine for disinfection. It is a widely used method all over the world, although dosages differ considerably. In Sweden the dosage limit and the maximum residual allowed are 1 mg/l Cl_2, SLV - Swedish National Food Administration (1993). Therefore, chlorine is not considered as a major parameter for solving existing corrosion problems.

2.3.5. Corrosion inhibitors

Corrosion inhibitors are used in some countries, but in Sweden for example, phosphate and silicate inhibitors are not allowed. Orthoposphates and phosphate/silicate-mixtures inhibitors reduce corrosion and iron uptake, Wagner and Kuch (1984) and Ryder and Wagner (1985). Silicates alone do not affect corrosion and polyphosphates alone raise both corrosion rate and iron uptake.

2.3.6. Organic material

Rudek (1979) showed that natural organic matter, NOM, can adsorb to calcium carbonate and consequently reduce the precipitation rate of calcium carbonate crystals. Slow precipitation improves the crystal line structure and the quality of the protective scale will be better. Iron(III)oxide, Fe_2O_3, is a catalyst of the oxidation of Fe^{2+} to Fe^{3+}. Rudek (1979), Larson (1966) and Sontheimer *et al.* (1981) show that humic substances adsorbed to iron(III)oxide delays this oxidation. Therefore, the corrosion rate decreases. Humic substances also change the crystallisation and precipitation rates of calcite, siderite and goethite. The effect of organic matter on the corrosion rate can be compared with that of high buffer capacity. Both promote the formation of siderite, Sontheimer *et al.* (1981). The hydrophobic part of humic acids can block surface groups on a mineral interface and inhibit dissolution, Stumm (1995).

Korshin *et al.* (1995) show that NOM affects the morphology of surface scales on copper, brass and lead (from highly-crystalline to amorphous organic-containing surface layers). Possibly this alteration of the morphology affects the redox-properties of the scales. Similar preliminary experiments to investigate the effect of NOM on black iron and galvanised steel were conducted, Ferguson *et al.* (1996). The release of soluble iron increased when NOM was added (2 mg/l as TOC, Total Organic Carbon) to Seattle tap water for both materials. This means that the corrosion problems might increase even if the corrosion rate decreases due to NOM adsorption.

2.3.7. Microorganisms

Microorganisms are present everywhere in the distribution net and can influence the corrosion rate. A prerequisite for microbial activity is a supply of organic material. A reduction of TOC reduces the amount of microorganisms, Schock (1990).

Hughes (1978) describe different ways that microorganisms affect the corrosion rate:
- direct chemical influence/action of metabolic products that microorganisms can secrete when they grow;
- microorganisms can cause local changes in oxygen potential, salt concentration, pH-value etc., which lead to the appearance of local corrosion cells;
- growth of microorganisms can decompose corrosion inhibitors or protective coatings;
- iron bacteria can oxidize iron(II) to iron(III), which they can build into tubercles or gelatinous biofilms. Those films can detach the water bulk and give red water.

Kölle and Rösh (1980) (in Sontheimer *et al.* (1981)) suggest that microorganisms hinder siderite formation partly through oxidation of iron and partly through reduction of sulphate to sulphide.

Hack (1986) describes, as an example of microbial induced corrosion, how a thin biofilm at the pipe wall prevents passivation of the iron surface. Periodic detachment of portions of the biofilm, due to abrupt changes in the water flow, alter the oxygen concentration in the biofilm. Parts that were anaerobic become temporarily aerobic and new nutrients are supplied to that area. The sulphur reducing bacteria that develop next to the wall can then reduce sulphate to sulphide and the area acts as the cathode. When another portion is detached, the cathode will move. This fluctuation between aerobic and anaerobic conditions seems to cause uniform corrosion over a long term.

Iron(II)ions from the corrosion pit in contact with sulphide ions form iron sulphide, which results in a black, gelatinous film around the corrosion site. In this environment iron-oxidizing bacteria thrive. Those microorganisms transform iron(II) into iron(II) hydroxide precipitates that cling to the filamentous structure of the bacteria. The tubercles then remain porous and nonprotective, Hack (1986).

2.3.8. Temperature

Temperature always influences the reaction rate, both in chemical and microbiological processes, this means the corrosion rate increases with increasing temperature. All salts, except calcium carbonate, are more soluble in water at a higher temperature. In hot water systems this means that the risk for clogging becomes more common when the temperature increases if the water is close to calcium carbonate saturation, Ryder and Wagner (1985) and Schock (1990). Diffusion of oxygen to the cathode increases with increasing temperature, since the viscosity of water is reduced and the diffusion constant increases. The growth rate for microorganisms significantly accelerates when the temperature exceeds 15-20 °C, Fransolet *et al.* (1985).

The temperature in the distribution net depends totally on the raw water source. If groundwater is used, the temperature is normally low and stable, in Sweden 6-10 °C, all year round, Knutsson and Morfeldt (1993). (Groundwater temperature reflects the annual atmospheric mean temperature.) The temperature of surface water varies with the location and the time of the year, in Sweden 0-20 °C.

2.3.9. Flow rate

The corrosion rate and other electrochemical reactions depend, as mentioned earlier, on the rate of transport of reactants, here oxygen, to the metal surface and of corrosion products from the surface to the bulk liquid, Snoeyink and Kuch (1985), Schock (1990) and Southampton Electrochemistry Group (1990).

Lind Johansson (1989) and, Fiksdal and Blekkan (1993) both showed that high flow velocities lead to a high corrosion rate if the conditions for development of a protective layer are missing. When a protective scale can has developed the flow rate is not decisive for the corrosion rate.

Variation between stationary and non-stationary conditions in the pipes means variation in the oxygen supply. In stagnant water oxygen will be depleted since both the corrosion reactions and microorganisms consume oxygen. The protective layer can then be weakened, by for example reduction to less adhesive products, Kuch and Sontheimer (1986), or microbiological activity, Hack (1986). It will dissolve or detach. The iron surface is then exposed to further corrosion.

According to Sontheimer *et al.* (1985) and Schock (1990) the diffusion of oxygen to the cathode determines the corrosion rate in stagnant water. An increase in flow velocity reduces the thickness of the diffusion layer and the diffusion rate of dissolved oxygen to the metal surface increases. Diffusion of oxygen also increases with increasing temperature since the viscosity of water is reduced and the diffusion constant increases. At high flow velocities, and no scale formation, the electron transfer is the rate determining step, Sontheimer *et al.* (1985), Schock (1990) and Southampton Electrochemistry Group (1990). When iron corrodes in drinking water a passive layer is formed and the different surface reactions become rate determining for the corrosion, Singley and Montgomery (1985) and Stumm (1995). Sander *et al.* (1996 a) and Sander *et al.* (1996 b) recently showed that the rate of iron corrosion depends on the nature and concentration of the surface complexes that form between the iron oxide surface and ions in bulk solution, for example hydrogen carbonate, carbonate and calcium. The flow rate had no influence on these processes.

2.4. *Models for corrosion*

Different models have been developed during the years to describe corrosion in drinking water and to facilitate corrosion control. None of the models have so far been able to explain all aspects of corrosion, but they are useful tools on the way to a more thorough understanding of corrosion.

2.4.1. Langelier index

The saturation index or Langelier index has been widely used after its introduction, Langelier (1936). This index, the Langelier Saturation Index ($LSI = pH - pH_s$), indicates if the water is supersaturated, $LSI>0$, or undersaturated, $LSI<0$, with respect to calcium carbonate, $CaCO_3$. Langelier meant that if the pH-value of the water was adjusted so it became slightly supersaturated, a thin film of $CaCO_3$ will precipitate on the pipe wall and protect the metal from further corrosion. The Langelier index is still in use, with some modifications of the different constants used, to calculate the saturation pH (pH_s) with respect to $CaCO_3$, calcite, Larson and Buswell (1942), Plummer and Busenberg (1982) and Schock (1984). Other corrosion indices, for example the Calcium Carbonate Precipitation Potential (CCPP) and the Ryznar Saturation Index (RSI) are also in use. The CCPP shows how much $CaCO_3$ in mg/l will either precipitate or dissolve. LSI and CCPP are calculated from pure equilibrium data, while the RSI is developed from empirical observations. For a review of the different corrosion indices Singley (1981), Rossum and Merrill (1983), Joint Task Group on Calcium Carbonate Saturation (1990), Schock (1984), Snoeyink and Kuch (1985) and Schock (1990) are recommended.

Stumm (1956), Larson and Skold (1957) and Schock (1984) showed that the Langelier index is insufficient to predict corrosion. Langelier index indicates the saturation for $CaCO_3$ as calcite, not how much $CaCO_3(s)$ will precipitate or if its structure will provide resistance to corrosion. If other forms of solid calcium carbonate are present, like aragonite, the water will appear supersaturated with respect to calcite, Schock and Neff (1982) (in Schock (1984)). Also, as iron corrodes the cathode reaction increases the pH-value at local corrosion sites, Stumm (1960) and Sontheimer *et al.* (1979). Hydroxide is formed when oxygen is reduced in the corrosion process, Eq. (1.2). This causes a local supersaturation of calcium carbonate, which can precipitate. Therefore precipitation can take place although the water as a whole is well below calcium carbonate saturation and has a negative Langelier index. When precipitation takes place small crystals can form on the iron surface and these can, in turn, act as nuclei for other corrosion products. A protective layer can therefore form faster in water containing calcium carbonate.

Ferguson (1985) points out that for many municipalities with low alkalinity waters, treating the water to achieve a positive Langelier index would be impossible, or even to come close to $LSI=0$. Partly because of the cost for chemicals and, partly because the pH-values would be too high, between 9 and 10.5.

2.4.2. The siderite model

Stumm (1960) and Sontheimer *et al.* (1979) showed that most waters are saturated with siderite ($FeCO_3$) well before saturation will be achieved for calcite. Siderite is decisive for formation of the shell-like layer of mainly pseudomorph goethite[1] (FeOOH) and magnetite (Fe_3O_4) in the scale. Kölle (1980) (in Sontheimer *et al.* (1981)) and Kölle and Rösh (1980) believe that this shell-like layer is the most protective part of the scale. Sontheimer *et al.* (1981) summarize the research results within the corrosion field at the University of Karlsruhe, Germany, including a description of the so-called siderite model. It should be noted that the conclusions are based on results from experiments with tap water from Karlsruhe ($Ca^{2+} \approx 80$ mg/l, alkalinity$\approx$300 mg/l HCO_3^-). Synthetic drinking water, with low or zero content of calcium, was used for some of the corrosion rate experiments, but all scales investigated were formed in tap water, that is, in hard water. The maximum pH for all waters was 8.5.

The siderite model is based on the following reactions:

Primary reactions:

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \qquad (2.1)$$

$$\tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^- \qquad (2.2)$$

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O \qquad (2.3)$$

Secondary reactions:

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3(s) \qquad \text{(calcite)} \qquad (2.4)$$

$$Fe^{2+} + CO_3^{2-} \longrightarrow FeCO_3(s) \qquad \text{(siderite)} \qquad (2.5)$$

$$2\,Fe^{2+} + \tfrac{1}{2}\,O_2 + 4\,OH^- \longrightarrow 2\,FeOOH(s) + H_2O \qquad \text{(amorphous goethite)} \qquad (2.6)$$

Tertiary reactions:

$$2\,FeCO_3(s) + \tfrac{1}{2}\,O_2 + H_2O \longrightarrow 2\,FeOOH(s) + 2\,CO_2 \qquad \text{(pseudomorph goethite)} \qquad (2.7)$$

$$3\,FeCO_3(s) + \tfrac{1}{2}\,O_2 \longrightarrow Fe_3O_4(s) + 3\,CO_2 \qquad \text{(magnetite)} \qquad (2.8)$$

Sontheimer concludes the following regarding corrosion in iron pipes:

- Different water qualities lead to different, relatively high corrosion rates when the pipes are new. After a few years the corrosion rate is low and almost independent of the inorganic components in all waters. The decisive factors between pipes with different corrosion tendencies are thickness and structure of the scales. Thick, porous scales can be a good environment for microorganisms and such scales can also easily detach and cause, for example, red water.

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[1] Pseudomorph goethite is formed by oxidation of siderite and retaining the stable crystal structure of siderite. This gives a denser structure than when goethite is formed directly from iron(II)ions (amorphous goethite - without a crystal structure, porous).

- Stable, dense and protective scales usually consist of divalent iron precipitates such as siderite, $FeCO_3$, and magnetite, Fe_3O_4. Concentrations of calcium carbonate, $CaCO_3$, exceeding 5 percent of the dry weight of the scales, give more irregular and less protective scales.

- Water with high chloride, nitrate and sulphate concentrations, a low concentration of humic substances and low buffer capacity causes most of the corrosion problems. Phosphates, as well as humic substances, lead to good protective layers that reduce the corrosion rate.

- The most important factor for the formation of good protective scales is the buffer capacity. High alkalinity gives high buffer capacity that subsequently leads to slower precipitation of corrosion products. Slow precipitation favours siderite to trivalent iron deposits, that is Eq. (2.5) over (2.6). Siderite is a requisite for the formation of a protective scale, even if it is not a part of the shell-like layer. Processes that interfere with siderite formation therefore increase the corrosion rate.

2.4.3. Kuch-type corrosion, iron uptake and the red water problem

Water quality problems are not caused by the corrosion itself but by the formation and dissolution of the corrosion products, Sontheimer *et al.* (1985). Calcium carbonate precipitations do not influence the appearance of red water. According to Sontheimer (1988) hydrogen carbonate reduces, while sulphate and different salts increase the red water problem.

Dissolution of corrosion deposits implies an underlying corrosion reaction, Figure 2.2. The two reactions do not have to proceed at the same rate, Ferguson (1985). The layer of corrosion products will alter between accumulation and dissolution and thus its characteristics change.

WATER	Metal Release or Uptake Reactions - Direct release - Scale dissolution - Scale dispersion	
SCALE OF CORROSION PRODUCTS	Secondary Reactions - Scale formation - Secondary oxidations - Reductions Primary Oxidation	Primary Reduction
METAL	Anode	Cathode

Figure 2.2 Chemical processes that are involved in the dissolution of corrosion products. After Ferguson (1986).

Kuch and Sontheimer (1986) describe how the formation of red water mainly is due to the variation between stationary and nonstationary conditions in the pipes, Kuch-type corrosion. The corrosion rate at the pipe wall is dependent on the oxygen supply. More oxygen is constantly provided to the pipe wall when the water is flowing. In stagnant water, or only slowly flowing, oxygen will be depleted since both the corrosion reactions and microorganisms consume oxygen. This causes the reduction of relatively stable iron(III) oxides, like amorphous goethite or lepidocrocoite, to less stable iron(II) hydroxides with less adhesive capacity, see reaction (2.9) from left to right. The iron(II) hydroxides will then be transported with the water, when the flow rate increases. This subsequently weakens the protective layer and the water can temporarily become red.

	The reaction path from left to right, $\longrightarrow$, is favoured under:	
$FeOOH(s) + H^+ + e^- \rightleftharpoons Fe(OH)_2(s) + H_2O$ amorphous goethite or lepidocrocoite $\rightleftharpoons$ iron(II)oxides	nonstationary conditions	(2.9)
$3\,FeOOH(s) + H^+ + e^- \longrightarrow Fe_3O_4(s) + 2\,H_2O$ amorphous goethite or lepidocrocoite $\longrightarrow$ magnetite	stationary conditions	(2.10)
$Fe_3O_4(s) + 2\,H^+ \rightleftharpoons Fe_2O_3(s) + Fe^{2}+ H_2O$ magnetite $\rightleftharpoons$ hematite	nonstationary conditions	(2.11)

Oxidation of ferrous iron (Fe^{2+}) to ferric (Fe^{3+}) is important during the development of scales, Stumm and Lee (1961), Sontheimer *et al.* (1981), Kuch and Sontheimer (1986) and others. Ferrous iron favours siderite formation. Stumm and Lee (1961) revealed that the oxidation rate is a first order reaction with respect to iron(II) ions and oxygen, and a second order reaction with respect to hydroxide:

$$-d[Fe^{2+}]/dt = k\,[Fe^{2+}]\,p(O_2)\,[OH^-]^2 \qquad (2.12)$$

In water with high alkalinity, $\geq$ 240 mg/l HCO_3^-, Jobin and Gosh (1972) showed that the buffer capacity, ß, has a definite influence on the oxidation rate of ferrous iron:

$$-d[Fe^{2+}]/dt = k\,[Fe^{2+}]\,p(O_2)\,[OH^-]^2\,[\beta]^{1/2} \qquad (2.13)$$

Sung and Morgan (1980) carried out oxidation rate tests with waters of various ionic strength (adjusted by $NaClO_{4)}$. They found that the oxidation rate is proportional to the square root of the ionic strength, when the pH-value is around 7 or below, and that this term should be added to Eq. (2.12). At higher pH-values they observed autocatalysis of ferrous iron oxygenation. Further investigations showed that the oxidation rate of ferrous to ferric iron is decreased by additions of sulphate, chloride, calcium and organic matter (varying between 10-500 mg/l), Jobin and Gosh (1972), Rudek (1979), Sung and Morgan (1980), Stumm and Morgan (1981) and Legrand and Leroy (1984).

The city of Göteborg used to have problems with red water in parts of the distribution system. Enander and Berghult (1994) report that increasing the alkalinity and the concentration of calcium (HCO_3^- from 18 to 60 mg/l and Ca^{2+} from 15 to 30 mg/l) led to a more stable water quality and fewer complaints from customers about red water. (However, the copper content in the wastewater sludge has increased since the change, Hedberg *et al.* (1995)). Hedberg *et al.* (1990) carried out an inquiry investigation in 143 Swedish municipalities that showed that red water problems, in the outer parts of the distribution system, were avoided when the water contained Ca^{2+} and HCO_3^- (at least 20 mg/l and 60 mg/l respectively) and as little organic substances as possible. Stumm (1960) showed that the corrosion rate decreased as the buffer capacity increased (exceptions were noted for water with LSI<-1.5 and "low" hardness, $Ca^{2+} \approx 70$ mg/l, (medium hard according to the Nordic terminology, SKTF (1953))). No waters with pH-values above 8.5 were studied. Pisigan and Singley (1987) found that the corrosion rate decreased with increasing buffer capacity, adjusted by changing the pH-values between 6-8.5. If, on the other hand, the buffer capacity was increased by changing the alkalinity, the corrosion rate increased, Pisigan and Singley (1987).

In very soft Norwegian water Fiksdal and Blekkan (1993) and Fiksdal (1995) found that the corrosion rate (as weight loss) decreased by up to 70% when the alkalinity was raised from 18 to 60 mg/l HCO_3^- and pH from 7 to 8.2, compared to the corrosion rate of raw water. If also the calcium content was increased, from 7 to 20, 30 and 40 mg/l Ca^{2+}, the rate reduction successively increased up to 90%. (When calcium was added, LSI became approximately -0.1, 0, +0.2 respectively.) Scale analysis showed that the content of $CaCO_3$ increased with increasing Ca^{2+} in the water. The lowest corrosion rate was observed with 30 mg/l Ca^{2+}. Small amounts of siderite were found in only one out of eighteen pipe scales investigated.

2.4.4. Surface reactions and surface complexes

Dissolution, precipitation and adsorption reactions on the surface determine whether a protective passive layer will develop or not on the iron surface. The composition and the properties of the passive layers are dependent on the surface reactions at the metal-water interface. These surface reactions cannot be explained by pure solution equilibria data. To reach an understanding of what controls the corrosion rate, surface complexation theory has to be considered, Stumm (1995).

Surface complexation theory is based on the idea that water molecules and dissolved species in the water form chemical bonds with exposed lattice-bound ions at mineral surfaces, Van Cappellen *et al.* (1993), Stumm (1987). Reviews of surface complexation theory can be found in several publications, Schindler and Stumm (1987), Westall (1987), Dzombak and Morel (1990), Stumm (1995) and Ahlberg (1995).

Surface complex formations are characterized by, Dzombak and Morel (1990):

- Surface complex formations take place at specific surface coordination sites.
- Surface complex formations can be described by mass law equations.
- Surface complex formations result in surface charge.
- Surface complex formations are affected by surface charge. To account for this effect a correction factor, derived from the electric double layer, should be applied on the mass law constants (the apparent complex formation constants corrected with respect to surface charge gives the intrinsic complex formation constants).

Surface complex formation constants describe to what extent the surface sites protonate/deprotonate, bind cations or anions and exchange their hydroxyl groups for other ligands, Van Cappellen *et al.* (1993). They have a linear correlation to corresponding complex formation constants in solution, Stone and Morgan (1987), Dzombak and Morel (1990), Ahlberg (1995) and Stumm (1995). Knowledge about the solution constants can therefore be used to estimate surface complexation constants.

Figure 2.3 shows hydration of a mineral surface, for example goethite. On the surface of iron a layer of iron oxide develops, goethite, and in water it will become hydrated. In pure water the solution pH controls if the surface hydroxyl groups are protonated or deprotonated. On goethite, in acid and basic water respectively, this means the formation of, Westall (1987):

$$>\text{Fe-OH}^0 + \text{H}^+ \longrightarrow >\text{Fe-OH}_2^+ \qquad (2.14)$$

$$>\text{Fe-OH}^0 \longrightarrow >\text{Fe-O}^- + \text{H}^+ \qquad (2.15)$$

$>\text{Fe-OH}^0$ means that an iron atom of the outermost layer of the surface forms a neutral surface complex with hydroxide originating from the water.

In drinking water dissolved anions or cations may adsorb at the mineral-water interface by exchanging H^+ or OH^- at surface sites, Stumm (1987).

Examples of anion surface complexation on goethite in a water containing carbonic acid or hydrogen carbonate, Stumm (1995):

$$>\text{Fe-OH}^0 + \text{H}_2\text{CO}_3 \rightleftharpoons >\text{Fe-HCO}_3^0 + \text{H}_2\text{O} \qquad (2.16)$$

$$>\text{Fe-OH}^0 + \text{HCO}_3^- \rightleftharpoons >\text{Fe-CO}_3^- + \text{H}_2\text{O} \qquad (2.17)$$

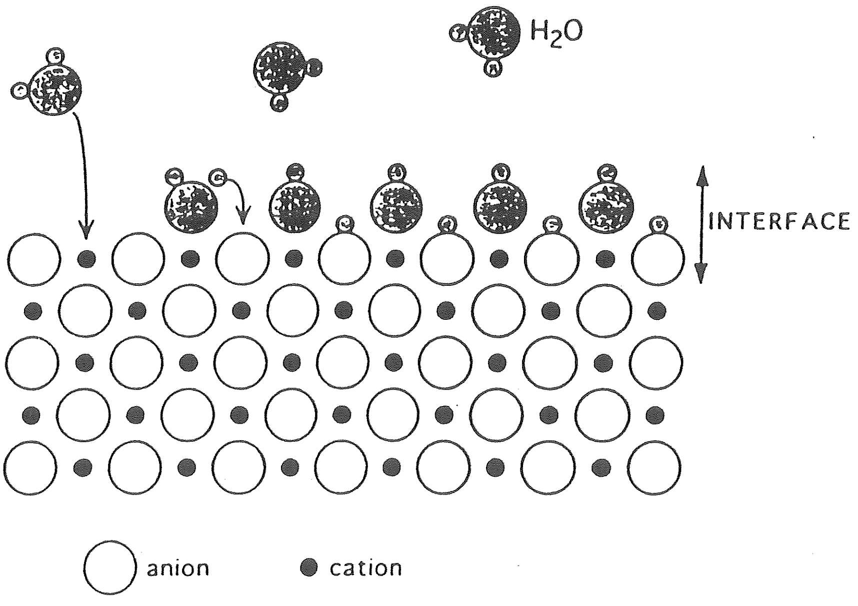

Figure 2.3 Hydration of a mineral surface. The hydration process leads to a surface composed of hydroxylated cation sites ($>Fe\text{-}OH^0$) and protonated anion sites ($>A\text{-}H^0$). After Van Cappellen et al (1993).

Free carbon dioxide (the sum of protonated carbonic acid and dissolved carbon dioxide) or hydrogen carbonate acts as a proton donor at surface hydroxide sites. The hydroxide group will leave as water and new surface complexes involving hydrogen carbonate can be formed. This increases the solubility of iron ions and facilitates the formation of siderite through deprotonation of the surface complex.

On a calcite surface, Van Cappellen *et al.* (1993):

$$>\mathrm{Ca\text{-}OH}^0 + \mathrm{H_2CO_3} \rightleftharpoons >\mathrm{Ca\text{-}HCO_3}^0 + \mathrm{H}^+ \qquad (2.18)$$

$$>\mathrm{Ca\text{-}OH}^0 + \mathrm{HCO_3}^- \rightleftharpoons >\mathrm{Ca\text{-}CO_3}^- + \mathrm{H}^+ \qquad (2.19)$$

Examples of cation surface complexation on goethite in water containing calcium, Dzombak and Morel (1990):

$$>\mathrm{Fe\text{-}OH}^0 + \mathrm{Ca}^{2+} \rightleftharpoons >\mathrm{Fe\text{-}O\text{-}Ca}^+ + \mathrm{H}^+ \qquad (2.20)$$

$$>\mathrm{Fe\text{-}OH}^0 + \mathrm{Ca}^{2+} \rightleftharpoons >\mathrm{Fe\text{-}OH\text{-}Ca}^{2+} \qquad (2.21)$$

Calcium complexation on goethite occurs at pH-values above 7, Ahlberg (1995). All cation sorption reactions are strongly dependent on the pH-value.

On a metal carbonate surface, for example calcite or siderite, the formation of carbonate-calcium complex:

$$>\mathrm{CO_3\text{-}H}^0 + \mathrm{Ca}^{2+} \rightleftharpoons >\mathrm{CO_3\text{-}Ca}^+ + \mathrm{H}^+ \qquad (2.22)$$

is strongly favoured over reactions (2.20) and (2.21), Van Cappellen *et al.* (1993).

Drinking water normally contains both anions and cations. These ligands will compete for the available surface sites and they will each hinder the adsorption of the other, Stone and Morgan (1987) and Stumm (1995). Ligand competition in water occurs between for example free carbon dioxide and calcium ions, Fig 2.4. In the presence of free carbon dioxide the hydroxide site will be replaced by hydrogen carbonate or carbonate, forming surface complexes of iron-hydrogen-carbonate or iron-carbonate. If the total carbonate content is low and calcium added, surface complexes such as iron-oxygen-calcium form.

The dissolution of an oxide can schematically be written, Stumm (1992), Stumm (1995):

$$\text{surface sites} + \text{reactants } (\mathrm{H}^+, \mathrm{OH}^-, \text{or ligands}) \xrightarrow{\text{fast}} \text{surface species} \qquad (2.23)$$

$$\text{surface species} \xrightarrow[\text{detachment of metal}]{\text{slow}} \text{metal (aq)} + \text{surface sites} \qquad (2.24)$$

The rate law of surface-controlled dissolution is based on the idea that:

- the attachment of the reactants to the surface sites is fast
- the following detachment of the metal species from the surface into the solution is slow and therefore rate-limiting
- the original surface sites are continuously reconstituted

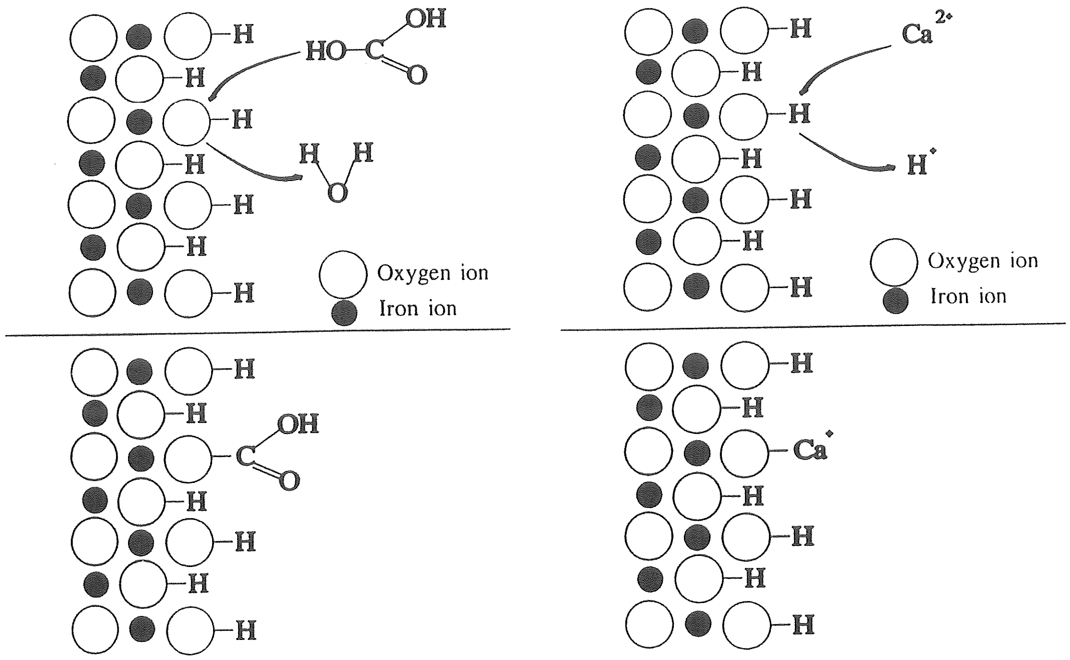

Figure 2.4 Adsorption of (a) the carbonate system or (b) calcium on goethite. From Sander et al (1996).

The dissolution rate is accordingly dependent on the surface species concentration, Stumm (1995). The surface species concentration depends on the relationship between the number of active surface sites and the solution concentration of the complexing agent.

Depending on whether the ligands are dissolution-promoting or dissolution-inhibiting the oxide will appear stable or dissolve. Dissolution-promoting ligands can weaken the metal-oxygen bonds in the lattice of the surface by altering the electron density. Bidentate ligands (ligands with two electron donor atoms), like dicarboxylates, hydroxycarboxylates, oxalate and salicylate, are effective in enhancing the dissolution rate. They alter the electron density at the surface so the metal-oxygen bonds in the crystalline lattice are weakened. Ligands that form binuclear surface complexes (bind to two centre metal ions in the surface lattice) generally inhibit dissolution, for example oxoanions like phosphate, silicates and borate.

The conditions for formation of protective scales on iron, with or without a considerable amount of calcite and/or siderite, were found to differ in water with different carbonate and calcium concentrations due to the competition for complex formation between carbonic acid and calcium, Sander *et al.* (1996 a), Sander *et al.* (1996 b). In the presence of free carbon dioxide, surface complexes of iron-hydrogen-carbonate or iron-carbonate form. If the total carbonate content is low and calcium added, surface complexes such as iron-oxygen-calcium form. At higher total carbonate and calcium concentrations complexes involving hydrogen carbonate or carbonate will dominate over the ones involving calcium. This will be discussed further in Chapter 4.

3. Experimental

Because of the electrochemical nature of corrosion, electrochemical techniques provide a convenient way to measure the rate of corrosion processes either in the laboratory or in the field, Nagy (1993). By electrochemical methods, both the anodic oxidation of the metal and the cathodic reduction of oxygen or hydrogen can be examined separately and thus a more detailed knowledge of the overall reaction is attained. Some advantages of electrochemical techniques are: (1) the measurements can be made very quickly; (2) an instantaneous or integrated (average) rate can be obtained; (3) the results are available as an electrical signal that can be easily transmitted, amplified or displayed; and (4) the measurements can be carried out, in most cases, with very little disturbance of the corroding surface.

To study the influence of the carbonate system and calcium concentration on the initial corrosion rate of iron in synthetic drinking water two different methods was used. One was an electrochemical method, slow scan potential dynamic sweep, PDS, and the other a weight loss method with iron coupons in stagnant water. From PDS measurements information about the mechanism can be obtained and with the coupons the resulting hypotheses can be confirmed. Field samples from 15 municipalities were used to verify that the theories are valid for genuine drinking water.

A computer model, SOLGASWATER, for surface and solution complex calculations, Eriksson (1979), was run to investigate whether the hypotheses are consistent with existing surface models and surface complexing constants for iron oxide at the iron surface in water containing the carbonate system and calcium.

3.1. PDS measurements: instrumentation, cells and electrodes

PDS with a rotating disc electrode, RDE, provides a convenient means of simulating flow conditions for electrochemical measurements in a controlled environment. The RDE gives a possibility to separate the effects of kinetics or coupled chemical reactions from those that arise from mass transport. During PDS, the electrode is assumed to be in pseudo-equilibrium at all potentials. The potential is varied slowly and linearly with time and the current density is recorded. Current density can be translated to corrosion rate by converting Amperes to moles per second, using Faraday's constant, and then via density to millimetres per year.

The slow scan potentiodynamic sweeps were carried out using a Hewlett Packard synthesizer 3325A and a Princeton Applied Research potentiostat/galvanostat 363. A Hewlett Packard multimeter 3478A collected the data and a Hewlett Packard microcomputer HP 85/86 controlled the system and analysed the data. The computer programs for system control and data analysis were developed by the electrochemistry group at the Department of Inorganic Chemistry, University of Gothenburg.

The electrochemical cell used, is shown in Figure 3.1. The cell consisted of a Metrohm titration vessel (150 ml) with a specially designed lid. The vessel was equipped with a rotating disc electrode device of our own manufacture as the working electrode. Rotating disc electrodes with a surface area of 0.2 cm^2, Figure 3.2, were prepared from pure iron rods 99.9985 % (Johnson Matthey Ltd). The electrodes were moulded in epoxy, exposing only

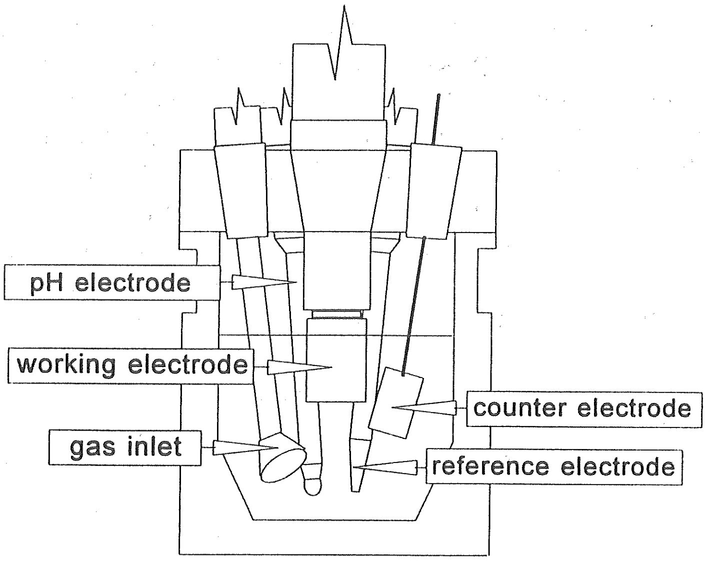

Figure 3.1 Electrochemical cell for rotating disc electrodes.

the circular disc surface. The potential of the working electrode was measured against a silver-silver chloride reference electrode (Ag/ AgCl, sat KCl, + 197 mV vs normal hydrogenelectrode, NHE). After each recorded sweep, the ohmic drop between the working and the reference electrode was measured and the potential was corrected with respect to this drop. The counter electrode was a cylindrical platinum net. All experiments were done at room temperature. The electrochemical system was run continuously under clean air.

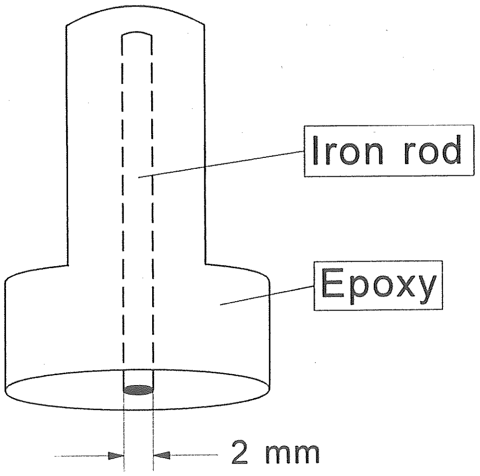

Figure 3.2 A disc electrode - an iron rod moulded in epoxy, exposing only the circular disc surface (diameter 0.2 cm^2).

The iron electrode was wet ground on 1000 mesh and 4000 mesh Carborundum papers (Struers), rinsed in double distilled water and immediately transferred to the electrochemical cell. In the cell the electrode was pretreated by a cycling procedure as follows: The scan was started at E = -350 mV vs Ag/AgCl, which is approximately the corrosion potential. A sweep was made in a positive direction, with a sweep rate of 5 mV/s, to E = 600 mV, reversed to E = -1000 mV and back to E = -350 mV. This procedure was repeated five times to achieve steady state conditions, before the scan was recorded.

Figure 3.3 is an example of a PDS voltammogram for iron in air-saturated synthetic drinking water, acid and slightly alkaline respectively. In acid water, pH below 6, active dissolution of iron takes place, while at higher pH-values the iron surface passivates due to film formation. At the cathodic side of the corrosion potential the current approaches a limiting plateau for oxygen reduction. The oxygen reduction showed a rotation rate dependence indicating a diffusion controlled process, Sander *et al.* (1996), while no dependence was observed on the anodic side for neutral or alkaline water. To estimate the corrosion rate the slopes of the anodic and cathodic curves are extrapolated to the corrosion potential. The diffusion controlled cathodic process did not affect the corrosion rate determination, which indicates that the corrosion rate appears to be independent of diffusion layer thickness and water flow velocity. The ohmic drop in the solution is difficult to determine and therefore the corrosion rate estimations are not precise. This leads to a slight spreading added to the uncertainty given by the system conditions.

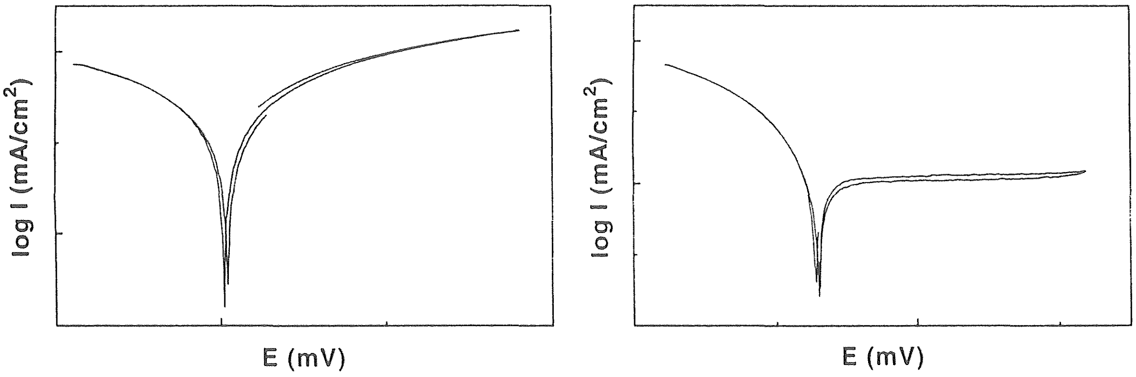

Figure 3.3 Typical sweeps for (a) active and (b) passive corrosion.

3.2. *Coupon tests*

Iron coupons were exposed to double distilled water with varying additions of hydrogen carbonate and calcium, in the same range as for the PDS measurements. Three test periods for 12-15 days were performed. The iron coupons were 22x37x2 mm^3 and made of pure iron. They were wet ground on 500 and 1000 mesh Carborundum papers (Struers), rinsed in ethanol in an ultrasonic bath followed by rinsing in double distilled water and immediately transferred to the beakers. The water was prepared in the same way as the electrolytes in the PDS measurements, see below. The beakers were mounted in a water bath holding constant temperature, 29.5 °C. (This temperature was chosen to ensure a constant temperature.)

Iron concentrations were analysed each day during the test period. The water volume was 400 ml at the start of the test. Each analysis of dissolved and total iron required between 0.5-10 ml of water. This volume decrease was accounted for when calculating the final iron concentrations. Before sampling the beakers were shaken.

Micropipettes, 200 and 5000 µl, were used to take out water samples from the beakers. The accuracy of the pipettes was ±1% (normally 0.6%) and the error of reproducibility $\leq$0.3%. A Hach instrument (DR/700 Colorimeter, Module 50.01) was used for iron analyses. The instrument gives accurate values between 0.02 - 5.0 mg/l Fe^{2+}. The iron content was never below 0.30 mg/l. Some samples had to be diluted to fit within the range of the analyser.

When stopping the tests, the iron content of the water was analysed, the water filtered (filter paper 00), the filtrate analysed, the corrosion products weighed and the total weight loss of the coupons measured.

3.3. Electrolytes

All experiments were carried out with synthetic drinking water as electrolytes. The electrolytes were prepared from double distilled water and sodium hydrogen carbonate ($NaHCO_3$, puriss, p.a.), concentrations between 0.5 mM and 10 mM. Clean air, in equilibrium with the electrolyte concentration of carbon dioxide, was bubbled through the electrolyte for thirty minutes to make the electrolyte saturated with respect to air. When pH was adjusted 0.1 M nitric acid (HNO_3, p.a.) and 0.5 M sodium hydroxide (NaOH, p.a.) were used.

In the coupon tests we used 0.1 M hydrochloric acid (HCl, p.a.) and 0.5 M sodium hydroxide to adjust pH. In order to have the same chloride concentrations in all beakers for the coupon tests, additions of sodium chloride (NaCl, p.a.) were made. Sodium was presumed not to influence the corrosion rate.

Calcium was added as calcium nitrate ($Ca(NO_3)_2$, puriss, p.a.) from 0.04 mM to close to saturation (with regard to $CaCO_3$) for each hydrogen carbonate concentration. Different concentrations of nitrates were tested and showed no effect on the corrosion rate within the range 0.05-0.25 mM.

The pH-values of the electrolytes were measured with a PHM84 Research pH meter (Radiometer Copenhagen) and a glass electrode (NaCl).

Migration and double layer effects have to be considered when electrochemical techniques are used in dilute solutions. The ionic concentration of the electrolytes varied between 2-36 mM. Ionic strength provided no direct correlation to the corrosion rate. An approximate calculation of the current distribution shows that less than 4% of the total current is carried by the reaction participants. Since the results follow the same trend as for the solutions with much higher ionic strength, the migration effect has been assumed to be of minor importance. For a clean surface determining the potential of zero charge is possible, but for a surface covered with a passive layer, this is impossible. Similar results between the PDS measurements and the coupon tests were taken as evidence for negligible double layer effects in the potential region used.

3.4. Field investigations

Samples were taken from six hydrants in fifteen Swedish municipalities and one Norwegian. To minimise the errors that sampling in a distribution network cause, a standard procedure was used. The selected hydrants were connected to iron pipes and chosen so that two were located at main pipes, two at the end of the distribution network and two between. Samples were taken four times (each season) in each municipality. To achieve reproducible results the hydrants were tapped at times of low consumption with a flow rate of 20 litres per second for 10 minutes before sampling, Enander (1990). The samples were analysed at a certified laboratory.

3.5. Theoretical calculations of surface and solution complexation

A computer program, SOLGASWATER, was used for calculations of the surface and solution complexation, Eriksson (1979). The reactions used and their constants are found in Table 3.1 and in Sander *et al.* (1996). Good estimations of the constants are available, for all but one, since the goethite surface has been thorougly studied, Sontheimer (1988), Dzombak and Morel (1990), Lövgren (1990), Gunneriusson (1993), Van Cappellen *et al.* (1993), van Geen *et al.* (1994) and Stumm and Morgan (1996). For one constant "best guess" is used. All reactions in the system are pH-dependent and the calculations were therefore made with pH as independent variable.

Estimations of the concentration of iron surface in the cell (0.2 cm^2/50 ml water) and in an iron pipe with a diameter of 200 mm (0.628 m^2/0.0314 m^3 water), give $6{,}7*10^{-10}$ M iron sites on the electrode in the electrochemical cell and $3.3*10^{-8}$ M iron sites on the pipe wall. (Assumptions: one iron site/$(nm)^2$; the roughness of the surface is compensated for by the fact that not all sites are active sites). For the complexation calculations a surface concentration of $1*10^{-8}$ M iron sites was used. However, as long as the concentration of iron surface is limiting in the system (10^{-8} M compared with approximately 10^{-3} M of hydrogen carbonate or calcium) no dependence was found for the complexing properties on the concentration of iron surface.

Table 3.1 Equilibrium reactions and constants used for SOLGASWATER calculations.
>Fe- – iron atoms in the goethite surface
>Fe-OH° – iron hydroxide surface complexes

Surface or solution reaction	log K	Eq. No	Reference
$H^+ + CO_3^{2-} \rightleftarrows HCO_3^-$	10.33	(3.1)	van Geen *et al.* (1994)
$2H^+ + CO_3^{2-} \rightleftarrows H_2CO_3$	16.68	(3.2)	van Geen *et al.* (1994)
$Ca^{2+} + H_2O \rightleftarrows CaO + 2H^+$	-12.6	(3.3)	Van Cappellen *et al.* (1993)
$Ca^{2+} + H^+ + CO_3^{2-} \rightleftarrows CaHCO_3^+$	11.59	(3.4)	Morel and Hering (1993)
$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3(s)$	8.42	(3.5)	Morel and Hering (1993)
$>Fe\text{-}OH^\circ + H^+ \rightleftarrows >Fe\text{-}OH_2^+$	7.47	(3.6)	van Geen *et al.* (1994)
$>Fe\text{-}OH^\circ \rightleftarrows >Fe\text{-}O^- + H^+$	-9.51	(3.7)	van Geen *et al.* (1994)
$>Fe\text{-}OH^\circ + Ca^{2+} \rightleftarrows >Fe\text{-}O\text{-}Ca^+ + H^+$	-5.85	(3.8)	Dzombak and Morel (1990)
$>Fe\text{-}OH^\circ + CO_3^{2-} + 2H^+ \rightleftarrows$ $>Fe\text{-}CO_3H^\circ + H_2O$	20.78	(3.9)	van Geen *et al.* (1994)
$>Fe\text{-}OH^\circ + CO_3^{2-} + H^+ \rightleftarrows$ $>Fe\text{-}CO_3^- + H_2O$	12.71	(3.10)	van Geen *et al.* (1994)
$>FeOH^\circ + CO_3^{2-} + Ca^{2+} + H^+ \rightleftarrows$ $>Fe\text{-}CO_3\text{-}Ca^+ + H_2O$	15.69	(3.11)	best guess

4. Results and discussion

The results have been reported and discussed in two papers, Sander *et al.* (1996 a) Appendix 1 and Sander *et al.* (1996 b) Appendix 2.

In the first paper, experimental results from the electrochemical measurements, the coupon tests and data from pipes in different municipalities are reported.

A surface complexation model is proposed to explain the dependence of iron corrosion on the carbonate system and the calcium content of the water. The second paper presents calculations on the surface complexation properties of the system and how they correlate with the experimental data. This chapter summarises the result sections of these two papers.

4.1. Experimental results

The initial corrosion rate, from PDS experiments, is shown as a function of the total carbonate content, Figure 4.1. At each concentration a wide range of corrosion rates was determined. However, high corrosion rates seem to correlate with high pH-values. This implies that total carbonate content is not determining for corrosion rate, instead certain components, protonated carbonic acid (H_2CO_3) and carbon dioxide (CO_2), are determining. In the following the combined concentrations of protonated carbonic acid and carbon dioxide will be referred to as free carbon dioxide. The initial corrosion rate seems to depend

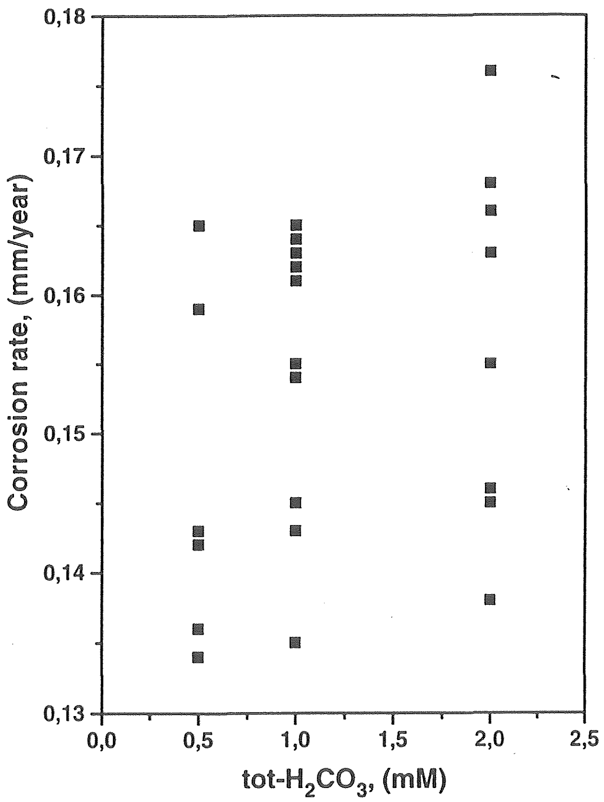

Figure 4.1 Corrosion rate estimations, using potential dynamic sweeps, as a function of total carbonate content for iron in air-saturated synthetic drinking water. pH-values are noted for each experiment.

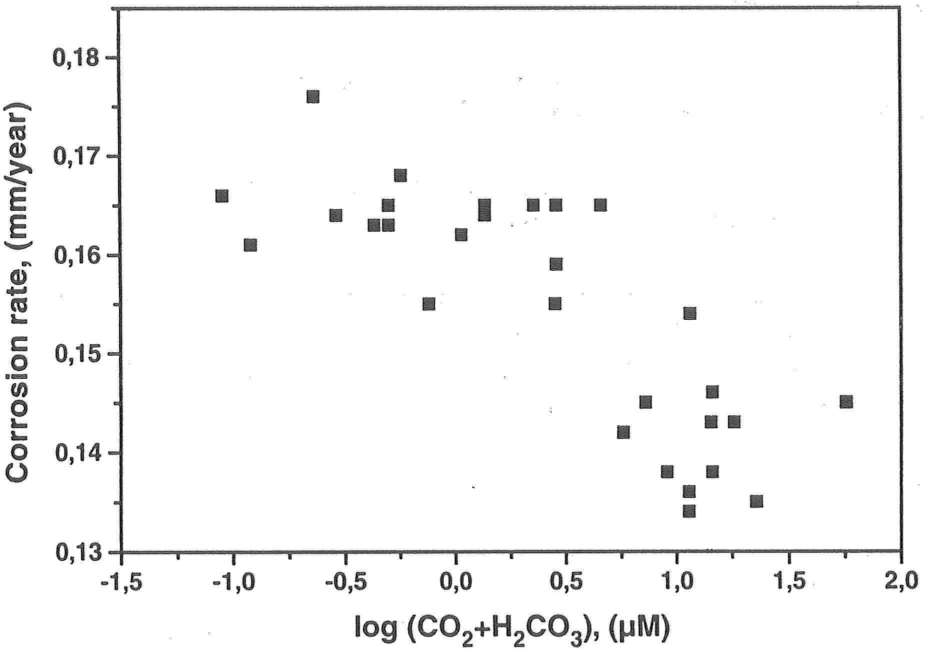

Figure 4.2 Corrosion rate estimations, using PDS, as a function of free carbon dioxide in air-saturated synthetic drinking water.

on the content of free carbon dioxide, Figure 4.2. A similar relationship, but expressed as loss of weight, was found for the coupon tests.

According to the siderite model, Sontheimer *et al.* (1981), the buffer capacity is the most important factor for stable protective layer formation. The Langelier protective layers of calcite, Langelier (1936) and Stumm (1956), would cause a corrosion rate dependence on the product of the calcium and the carbonate ion content. No clear dependence on the buffer capacity or the product of the calcium and the carbonate ion content can be seen from this investigation. Of course this does not exclude siderite as an important corrosion product during film formation.

Calcium content is often referred to as an important factor for iron corrosion, Langelier (1936) and Fiksdal and Blekkan (1993). In this investigation calcium affected the corrosion rate in very soft waters but, as can be seen from Figure 4.3, at higher total carbonate concentrations the effect of calcium disappears. This agrees with the results discussed by Sontheimer *et al.* (1981) and Fiksdal and Blekkan (1993) where calcite layers are observed in waters with low calcium and total carbonate concentrations. However, the explanation based on pure solution equilibria data does not seem sufficient. Instead, the corrosion rate dependence can be interpreted in terms of surface complexation. The effect of free carbon dioxide on surface complexation at an iron mineral has been considered by for example Wieckowski *et al.* (1983), Van Cappellen *et al.* (1993) and Stumm (1995). A schematic representation of the surface reaction on iron is shown in Figure 2.4. Free carbon dioxide acts as a proton donor at surface hydroxide sites. The hydroxide group will leave as water and new surface complexes involving hydrogen carbonate can be formed. This increases the solubility of ionic iron and promotes the formation of siderite through deprotonation of the surface complex.

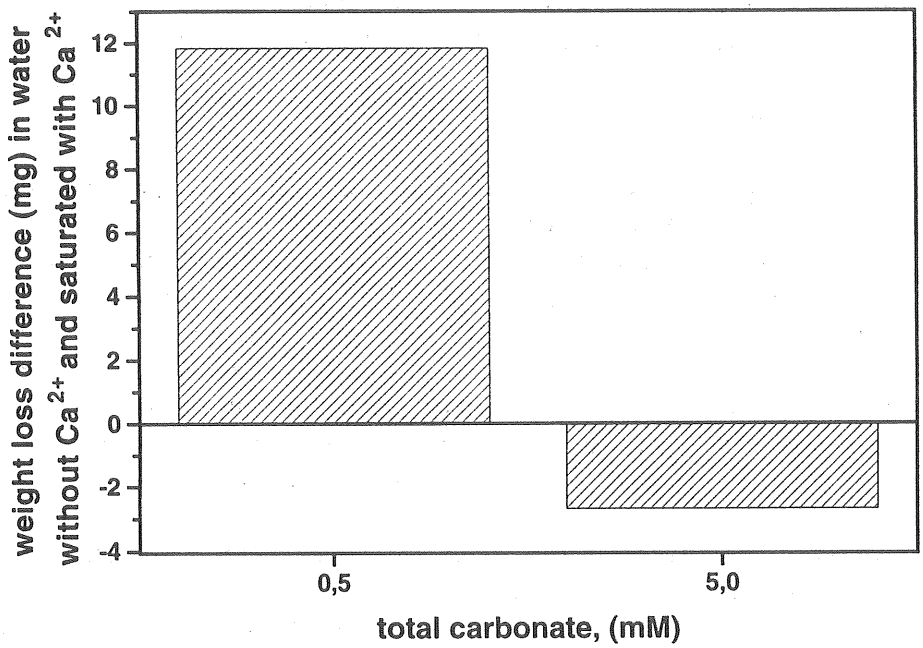

Figure 4.3 The influence of calcium concentration on corrosion rate in water with different total carbonate content.

In the calcium case several surface complexes are possible on the iron hydroxide surface. The most likely inner sphere complex is presented in Fig. 2.5. Surface complexation with free carbon dioxide causes dissolution of formed calcite, Van Cappellen *et al.* (1993). This can be a possible explanation for the absence of calcium effects in waters with high alkalinity and hardness. In soft waters the formation of calcium carbonate surface complexes can dominate over the iron carbonate surface complexes due to thermodynamic properties. Thus, a calcite protective layer can be formed if the free carbon dioxide content is low enough not to cause calcite dissolution. A further conclusion would be that the linear relationship in Figure 4.1 might not be extrapolated to a low free carbon dioxide content. This area would instead show a dependence on the calcium concentration.

According to the surface complexation model discussed above one would expect a pH variation in the water from the coupon tests. In the soft water (0.5 mM total carbonate content) saturated with calcium, the calcium surface complex would lead to a pH decrease and this was also observed. In waters with high total carbonate content (5 mM), with and without calcium, a pH increase should be expected and was noticed. Only little surface complexation involving carbonate calcium would be expected in the case with soft water and no calcium. No change of the pH values was observed.

Sontheimer *et al.* (1981) stress the importance of slow corrosion product precipitation to form corrosion products attached to the pipe wall. Less corrosion products are then transported with the water and water quality problems at the consumers' taps are reduced. The mechanism involves siderite formation. Looking at the corrosion product precipitation as a competition between surface complexes of free carbon dioxide and calcium ions, the former would be the one to prefer according to the siderite model. Results from field measurements in a number of Swedish municipalities and one Norwegian show that the municipality with the lowest alkalinity has the least problems with water quality deterioration (due to low calcium content and high content of free carbon dioxide).

4.2. Theoretical calculations

Calculations on surface complexing properties have been made for the system, consisting of a goethite surface (iron oxide) and water with different concentrations of total carbonate and calcium. Figure 4.4 and 4.5 show how the different surface complexes and calcite vary with pH for a soft (0.4 mM Ca^{2+}) and a harder (2 mM Ca^{2+}) water. The total surface concentration was set to $1*10^{-8}$ M iron sites, see Chapter 3.5. Different surface species dominate depending on the pH-value and the water quality. For calcite to start to precipitate, the pH-value must be about 8.7 in the low alkalinity water and only slightly above 7 in the high alkalinity water. It can be seen in the figures that the complex formations for some species are affected when calcite precipitation takes place.

Two explanations are possible for the surface complex interaction on the corrosion process. One is that the surface complexes dissolve the oxide at the surface, see Chapter 2.2, the other that the corrosion reactions proceed through pores and cracks in the oxide film. In the dissolution case, iron ions will form passivating corrosion products and a steady state situation may be reached. The corrosion rate would here be proportional to the dissolution rate of the corrosion products. When instead, the corrosion proceeds through the oxide layer, the corrosion rate is dependent on the physical, chemical and electrochemical properties of the surface complexes.

Both mechanisms can occur at the same time. On a long term basis the mechanism with corrosion through the oxide layer seems to be dominating.

4.3. The surface complex model applied to electrochemical measurements

Applying the surface complex model to the electrochemical data showed a correlation between the corrosion rate and the sum of surface complexes not involving calcium. The hydrated complexes $>FeOH_2^+$ and $>FeHCO_3$ were less dominant than the other complexes. As mentioned in Chapter 2.2, surface complexation may promote dissolution of the oxide layer. Under the assumption that the corrosion mechanism involving oxide dissolution is dominating, even lower contribution from these hydrated complexes would be expected due to the power exponent in the rate expression for proton-promoted dissolution, see Sander *et al.* (1996 b) Appendix 2. This shows that either the mechanism with corrosion through the inhomogeneous oxide layer or both mechanisms determines the initial corrosion rate. Calcium complexes seem to inhibit the surface, indicating a lower dissolution rate for these complexes. In order not to over-interprete the results only linear terms were applied for the interpretation, giving an approximate rate function according to Equation 4.1:

$$r_{corr} \propto [>FeOH] + [>FeO^-] + [>FeCO_3^-] + 0.8([>FeOH_2^+] + [>FeHCO_3]) \qquad (4.1)$$

In Figure 4.6 the normalised experimental results and the theoretical data for different total carbonate concentrations are plotted together as a function of the logarithm of the free carbon dioxide content. The mean error and the error standard deviation, in percent of the difference between the highest and the lowest experimental data in Figure 4.6, are 11.7

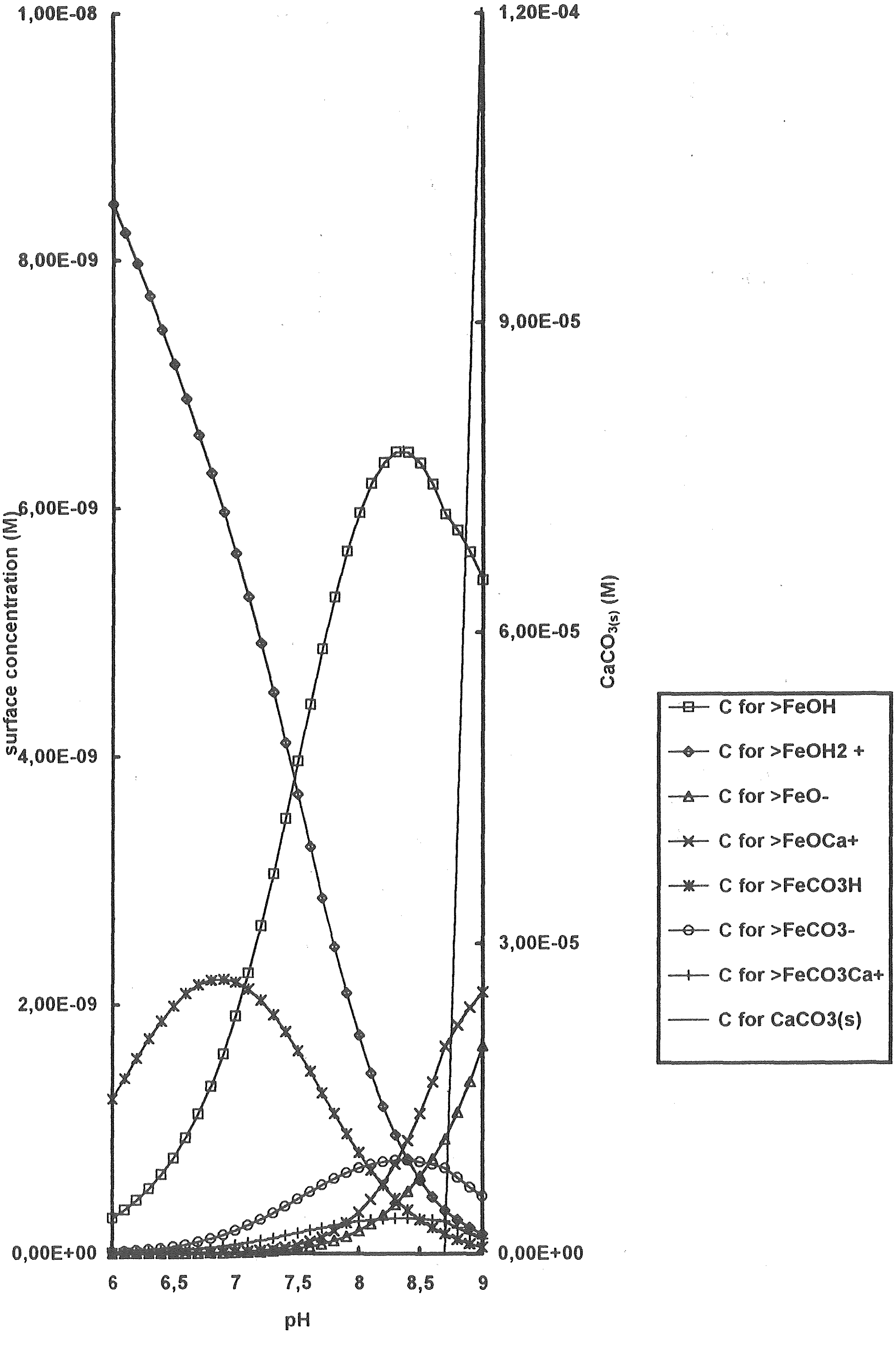

Figure 4.4 Surface complex concentration as a function of pH for a typical soft water with 0.5 mM total carbonate concentration and 0.4 mM calcium content and The concentration of solid calcium carbonate is plotted on a separate axis.

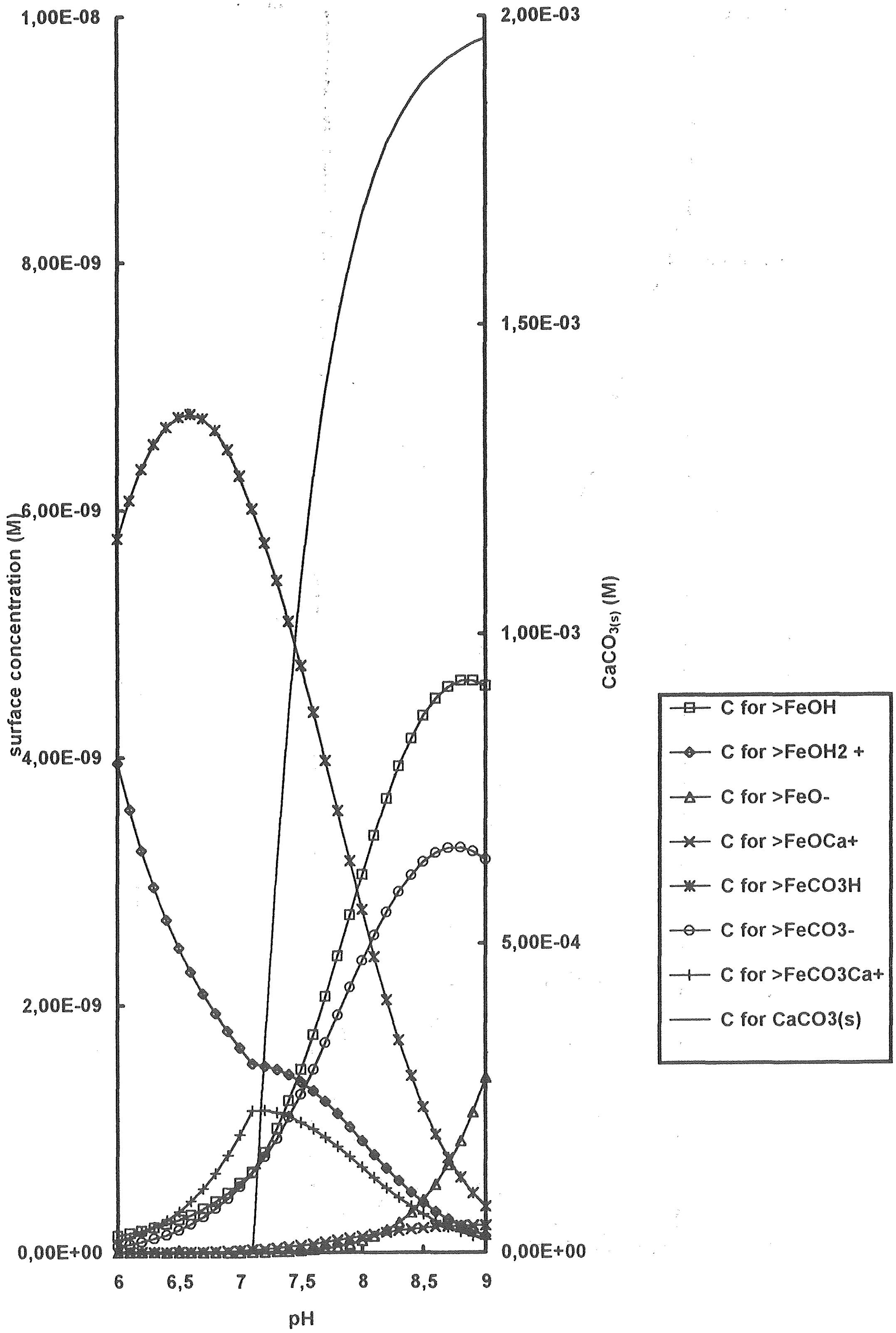

Figure 4.5 Surface complex concentration as a function of pH for a harder water with 5 mM total carbonate concentration and 2 mM calcium content. The concentration of solid calcium carbonate is plotted on a separate axis.

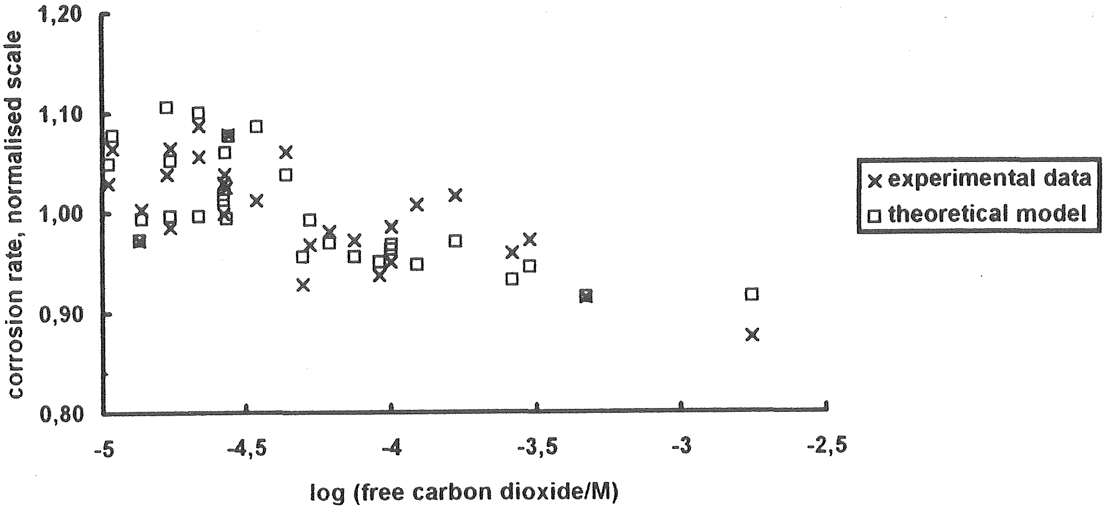

Figure 4.6 Normalised corrosion rate and theoretical model as a function of the free carbon dioxide concentration for different total carbonate concentrations with varying calcium content plotted together.

and 14.8, respectively. Thus, this rate function is not claimed to be the best theoretical approximation for the system, but it clearly shows the applicability of the surface complex model on this system.

4.4. The surface complex model applied to field measurements

In the field measurements the corrosion product released to and transported with the water is measured. This release may primarily depend on the dissolution and precipitation properties of the corrosion products. Therefore, another theoretical function than for the initial corrosion has to be applied. The inside surfaces of the iron pipes along a distribution network are covered with corrosion products to a different extent. Corrosion can proceed in two different ways, as discussed in Chapter 4.2. Either the surface complexes dissolve the oxide layer and expose the surface to further corrosion, or the corrosion proceeds through the inhomogeneous oxide layer. Since most complexes seem to inhibit further corrosion, it is likely that the dominant corrosion mechanism involves corrosion through the oxide layer. During the corrosion process Fe^{2+} ions are produced and siderite can be formed. The siderite may be better attached to the surface than the oxide or may be the initial product for further oxidation to stable oxide products, as discussed by Sontheimer *et al.* (1981), Kuch (1985), Kuch (1988) and Sontheimer (1988). The current model does not exclude this possibility or the action of calcite for the formation of protective corrosion product layers in low alkalinity waters. A possibility is that the products are formed through the action of surface complexes. However, corrosion product release to the water does not seem to depend on these products. Instead further corrosion through pores and cracks in the oxide layer depend on two surface complexes that are not as protective as the other complexes:

$$r_{corr} \propto [>FeOH] + [>FeCO_3Ca^+] \tag{4.2}$$

If this relation is true, the corrosion product release in a steady state situation is a measure of the corrosion rate in the distribution system and very little corrosion products will remain in the pipes for a long time.

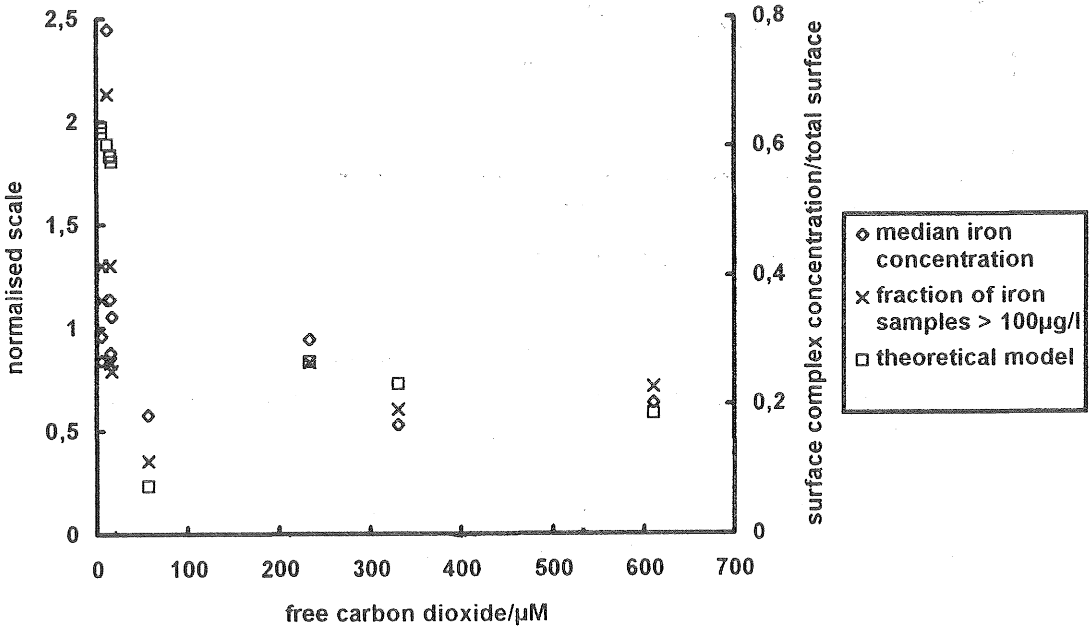

Figure 4.7 Normalised statistic evaluation of iron samples from different municipalities and the theoretical model as a function of the free carbon dioxide concentration.

In Figure 4.7 the median of iron samples in each municipality, the fractions of iron samples exceeding 100 mg/l and the theoretical model, Equation 4.2, are plotted versus the free carbon dioxide content. At low free carbon dioxide concentrations the values of the theoretical function have higher values than the measured ones. However, it is well known that corrosion products formed in large dimension pipes will remain on the pipe bottom until the system is flushed due to high consumption or pressure disturbance.

4.5. The surface complex model applied to coupon tests

The amount of total corrosion products produced in the coupon tests would be expected to follow the same theoretical expression as was found in the networks. Except for two coupons, which were affected by pitting corrosion, the coupon data fitted well into the model.

It is interesting that the total amount of corrosion products matches the theoretical function, not the amount released to the water. This implies that the network situation is at steady state, and that most of the corrosion products will evevtually reach the consumers.

4.6. Consequences of the surface complex model

The rate expressions for the initial corrosion rate on iron and the steady state corrosion rate in the distribution system are not claimed to be the truth. It is though interesting how well the theoretical expressions fit real data. Since no other explanation is available that fit the system better, some speculations can be made on the basis of these expressions. The initial corrosion rates for two different total carbonate concentrations are plotted versus pH in Figure 4.8. A third independent variable, the total calcium content is introduced. Calcium clearly reduces the initial corrosion rate in the low alkalinity water at high pH-values. For the high alkalinity water calcium hardly affects the corrosion rate. When the water contains no calcium, the initial corrosion rate is almost independent of the total carbonate concentration.

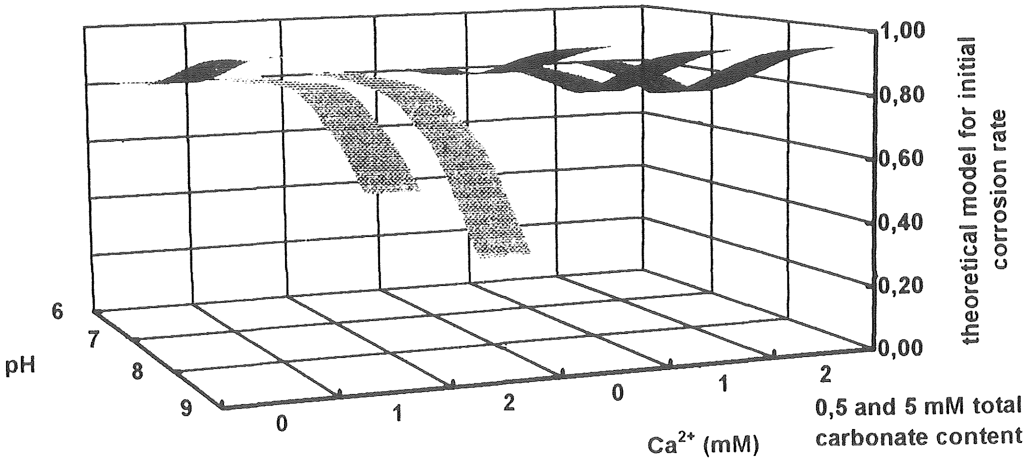

Figure 4.8 Theoretical model for the initial corrosion rate versus pH and calcium content for two total carbonate concentrations, 0.5 and 5 mM.

In Figure 4.9 the rate expressions for the network situation (or coupon tests) are plotted for the same waters. Here it can be seen, that low pH would yield low corrosion rates for all waters. Calcium has a reducing effect in the low alkalinity water and also in the network situation. However, in the high alkalinity water the corrosion rate slightly increases with the calcium content.

Low pH-values would be interesting if only iron pipes were present in the distribution system. Today other materials, such as concrete and copper, are present as well. Both concrete and copper pipes require higher pH-values, around eight to nine, if deterioration is to be prevented. However, an increase of the calcium content in low alkalinity waters and a decrease in high alkalinity waters would yield a slightly better situation regarding iron corrosion at high pH-values.

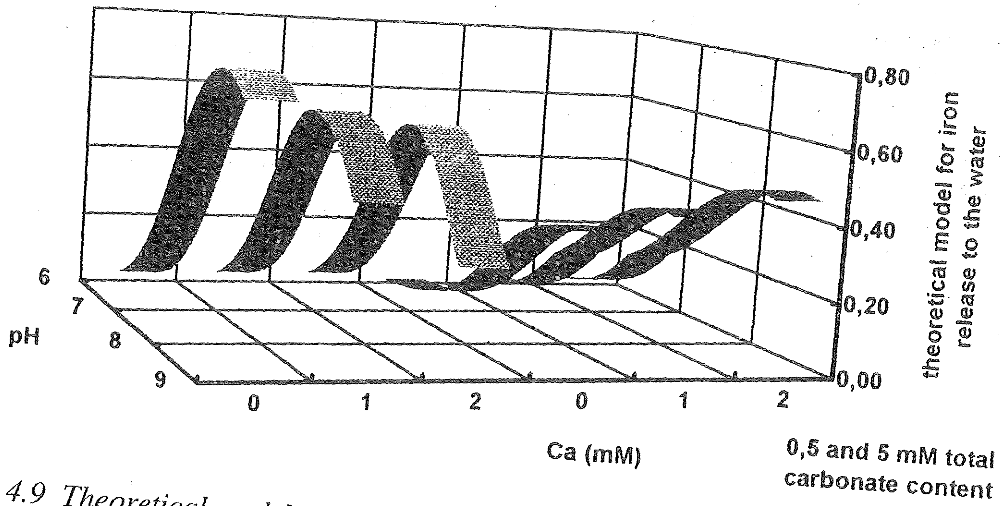

Figure 4.9 Theoretical model for the corrosion rate (and the iron content of the water) in a network versus pH and calcium content for two total carbonate concentrations, 0.5 and 5 mM.

5. Conclusions

A surface complex model is proposed to describe initial iron corrosion and corrosion products released in drinking water.

- The surface complex model evidently presents a convenient way of expressing iron corrosion in drinking water systems.

- In waters with moderate or high total carbonate concentrations surface complexes are formed from free carbon dioxide. In waters with low total carbonate concentrations the surface complexes involves calcium. At low total carbonate concentrations the corrosion rate is dependent on the calcium content while at high total carbonate concentrations no dependence is observed.

- A reversed proportional relationship between the logarithm of the free carbon dioxide content and the corrosion rate is observed.

- Initial corrosion rate at an iron surface in drinking water possibly proceeds through pores in the oxide structure. Depending on the surface complexes, the corrosion will proceed or be almost inhibited.

- The corrosion in the networks does not follow the same rate expression as the initial corrosion rate.

- Formation of siderite or, at higher pH-values, calcite may take part in producing stable and dense corrosion product layers at the pipe wall, but does not need to affect the corrosion process.

- It is likely that the situation in the networks is at steady state, where both the corrosion rate and the corrosion product release to the water follow the same expression dependent on the dissolution/precipitation properties of the corrosion products.

6. For the future

This report covers only iron as pipe material and a few water quality parameters concerning the drinking water system. Consequently, other pipe materials and more parameters influencing the corrosion processes need to be studied to understand the whole system. A final report for the project will be published during 1996 including iron and copper pipes and the influence of the different components on the carbonate system and the calcium concentration on the corrosion processes.

In the future it will be necessary to understand how organic matter influences the corrosion processes. Organic matter is involved in surface reactions and competes with other water quality parameters for the surface sites. Furthermore, organic matter largely influences microbiological activity in drinking water networks.

The water quality entering the distribution network may be altered at the treatment plants to improve water quality and/or the corrosion situation or, when introducing a new water source. Understanding and predicting how water quality changes will affect the corrosion situation and the water quality for existing pipes and already developed scales are very important.

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