ANNEX VII | 8DHC-05.05

IEA DHC|CHP

International Energy Agency
IEA Implementing Agreement on District Heating and Cooling,
including the integration of CHP

BIOFOULING AND MICROBIOLOGICALLY INFLUENCED CORROSION IN DISTRICT HEATING NETWORKS

International Energy Agency

Programme of Research, Development and Demonstration on District Heating

Biofouling and Microbiologically Influenced Corrosion in District Heating Networks

International survey covering fouling and corrosion in ten different district heating systems

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Preface and Acknowledgements

The International Energy Agency (IEA) was established in 1974 in order to strengthen the co-operation between member countries and reduce the dependency on oil and other fossil fuels. Thirty years later, the IEA again drew attention to serious concerns about energy security, investment, environment and energy poverty. The global situation is resulting in soaring oil and gas prices, the increasing vulnerability of energy supply routes and ever-increasing emissions of climate-destabilising carbon dioxide.

The IEA's World Energy Outlook "Reference Scenario" 2004 projects that, in the absence of new government policies or accelerated deployment of new technologies, world primary energy demand will rise by 59% by 2030, with 85% of that increase from the use of coal, oil and natural gas. However, these trends are not unalterable. The World Energy Outlook "Alternative Policy Scenario" shows that more vigorous government action and accelerated deployment of new technologies could steer the world onto a markedly different energy path, where world energy demand would be 10% lower and carbon-dioxide emissions 16% lower.

DHC makes a difference
One of the key technologies that can make a difference is District Heating and Cooling. DHC is an integrative technology that can make significant contributions to reducing emissions of carbon dioxide and air pollution and to increasing energy security.

The fundamental idea of DHC is simple but powerful: connect multiple thermal energy users through a piping network to environmentally optimum energy sources, such as combined heat and power (CHP), industrial waste heat and renewable energy sources such as biomass, geothermal and natural sources of heating and cooling.

The ability to assemble and connect thermal loads enables these environmentally optimum sources to be used in a cost-effective way, and also offers ongoing fuel flexibility. By integrating district cooling carbon-intensive electrically-based airconditioning, rapidly growing in many countries, can be displaced.

As an element of the International Energy Agency Programme, the participating countries undertake co-operative actions in energy research, development and demonstration.

One of the programmes that has run for more than 25 years is the Implementing Agreement 'District Heating and Cooling including the integration of Combined Heat and Power'.

Annex VII
In May 2002 Annex VII started.

List of the recent research projects (annexes) undertaken by the District Heating & Cooling Implementing Agreement. Ten countries participated from Europe, North America and Asia: Canada, Denmark, Finland, Germany, Korea, The Netherlands, Norway, Sweden, United Kingdom, and United States.

Project title	Company	Project number
A comparison of distributed CHP/DH with large-scale CHP/DH	Parsons Brinckerhoff Ltd, formerly PB Power Ltd – Energy Project leader: **Paul Woods**	8DHC-05.01
Two-step decision and optimisation model for centralised or decentralised thermal storage in DH&C	SP Swedish National Testing and Research Institute Project leader: **John Rune Nielsen**	8DHC-05.02
Improvement of operational temperature differences in district heating systems	ZW Energiteknik Project leader: **Heimo Zinko**	8DHC-05.03
How cellular gases influence insulation properties of district heating pipes and the competitiveness of district energy	Danish Technological Institute Project leader: **Henning D. Smidt**	8DHC-05.04
Biofouling and microbiologically influenced corrosion in district heating networks	Danish Technological Institute Project leader: **Bo Højris Olesen**	8DHC-05.05
Dynamic heat storage optimization and Demand Side Management	Fraunhofer Institut Umwelt-, Sicherheits-, Energietechnik UMSICHT, Project leader: **Michael Wigbels**	8DHC-05.06
Strategies to manage heat losses – Technique and Economy	MVV Energie AG Technology and Innovationsmanagement Project leader: **Frieder Schmitt**	8DHC-05.07

Benefits of membership
Membership of this implementing agreement fosters sharing of knowledge and current best practice from many countries including those where:

- DHC is already a mature industry
- DHC is well established but refurbishment is a key issue
- DHC is not well established.

Membership proves invaluable in enhancing the quality of support given under national programmes. Participant countries benefit through the active participation in the programme of their own consultants and research organisations. Each of the projects is supported by a team of experts, one from each participant country. As well as the final research reports, other benefits include the cross-fertilisation of ideas which has resulted not only in shared knowledge but also in opportunities for further collaboration.

New member countries are very welcome – please simply contact us (see below) to discuss.

Information
General information about the IEA Programme District Heating and Cooling, including the integration of CHP can be obtained from our website www.iea-dhc.org or from:

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Acknowledgement
This report concludes the project "Biofouling and Microbiologically Influenced Corrosion in District Heating Networks", an international survey covering fouling and corrosion in ten different district heating systems.

The work has been conducted by the Danish Technological Institute, Department of Chemistry and Water Technology located in Aarhus, Denmark. The project has been monitored by an IEA-Experts Group consisting of the following experts:

Mr. Veli-Pekka Sirola
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Mr. Jan Elleriis
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Denmark

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United Kingdom

The Swedish Corrosion Institute located in Stockholm, Sweden was subcontractor on the project and dealt with the exposure of metal samples under stagnant conditions and localised electrochemical analysis.

The project leader, Bo Højris Olesen at the Danish Technological Institute, wishes to thank all the persons who have been involved in the completion of this project. In particular the engagement of people at the involved district heating plants and the help from Henrik Koch and others at Aalborg University has been highly appreciated.

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Content

1 Summary

As a reflection on several recent cases of Microbiologically Influenced Corrosion (MIC) in Danish district heating systems, a preliminary survey on biofouling, corrosion, and corrosion mechanisms has been performed throughout selected DH plants within the IEA member countries. Emphasis has been put on evaluation of MIC in the involved plants.

10 plants have participated in the survey:

- Budapest, Hungary
- Lienz, Austria
- Lemgo, Germany
- Southampton, United Kingdom
- Helsinki, Finland
- Děčín, Czech Republic
- Stockholm, Sweden (two plants: Hässelby and Värtan)
- Aarhus, Denmark (two plants: Transmission and Distribution)

Among these plants general corrosion rates ranging from 1 to 40 micrometer/year was recorded. The amount of biofouling in terms of total number of cells on the surface was within the range of 10^3 to 10^7 cells/cm^2. Measurements of pitting attacks showed local corrosion rates ranging from no localised corrosion to 400 micrometer/year. A calculated pitting factor, based on the relation between general and local corrosion rates, ranged from 0 to 70. A pitting factor of 70 means that the localised corrosion rate is 70 times higher than the general corrosion rate.

In Budapest a high general corrosion rate of initially 38 µm/year (reduced to 16 µm/year after 6 months exposure) is not thought solely to be a result of MIC, but rather an effect of a constantly high concentration of oxygen in the water. There are signs of MIC so the overall corrosion reaction may be a combination of oxygen and MIC.

In Lienz and the two plants in Aarhus, the corrosion rate was very low (less than 3 µm/year) and no evidence of MIC was found.

In Helsinki the use of hydrazine is assumed to have limited the presence and activity of bacteria to an extent where MIC is less probable. The rather unique water quality in Helsinki has though caused some form of localised corrosion to occur.

In Lemgo and Southampton there is positive evidence that bacteria are influencing the corrosion processes. The bacterial number is high, the general corrosion rate is low but the local corrosion rate is high. Local corrosion attacks were associated with the presence of solid sulphur compounds probably in the form of iron sulphides. All these facts point towards MIC.

In Hässelby and to some extent in Värtan too the situation is somewhat the same. However, it seems that the corrosion process besides being influenced by bacteria is affected by what appears to be fluctuating oxygen content in the water.

At the plant in Děčín signs of MIC initiation are beginning to show. However, the process seems to be taking on quite slowly, and thus it is not possible to make a clear diagnosis at the moment.

A critical evaluation of the various analytical methods used to address biofouling and corrosion in the survey is presented. Of the two coupon exposure methods used, one simulated pipe flow within a unit impermeable to oxygen, whereas the other can be said to simulate stagnant water in a unit made of PVC which must be assumed to be permeable to oxygen to some extent.

Exposing the coupons in the stagnant water unit is assumed to cause an overestimation of the corrosion rate due to the oxygen penetration into the unit. On the other hand, the lack of flow within the unit may decrease the effect of oxygen and increase the effect of MIC.

Enumerating bacteria by growth-based methods has proven to be inadequate to evaluate biofouling in district heating systems. Total bacteria counts provide a more accurate measure. However, it should be noted that only one of the two methods for total counts covers a sufficient range of fouling degree to describe fouling in DH systems. A method where the bacteria are stained, transferred to a filter and counted applying epi-fluorescence microscopy proved to be the best available technique.

The corrosion methods applying weight loss as a measure of general corrosion particularly when associated by local rate measurements, have proven to be a strong technique. Besides corrosion rates, information on shape of local attacks (e.g. pinholes) may also be extracted from the topographical data.

As another part of the project, a number of new and promising techniques have been evaluated for use in MIC investigations. X-ray fluorescence particularly when used in a mapping mode, gave detailed information on the distribution of elements around corrosion sites. As an example sulphide on coupons from Southampton was shown to be concentrated within elongated tubercles on the surface, whereas sulphide on coupons from Hässelby was found to be spread out.

A method for identifying specific bacteria (FISH) was tested on SRB from selected coupons. The results were not very positive as it was not possible to perform the analysis directly on corroded samples and thus yield information on the spatial relationship between corrosion and bacterial species. Trying the method on biofilm removed from the corroded coupons turned out better, but problems occurred when too many corrosion products were present. Thus the best results were obtained for biofilms scraped from uncorroded stainless steel coupons.

Localised corrosion reactions were sought identified applying a number of localised electrochemical methods. The slight curvature of the coupons made it impossible to perform the micro-scale techniques. Electrochemical impedance spectroscopy, one of the localised methods, were instead applied on a macroscopic level to two sets of coupons illustrating the power of the method, given the problem with curvature is solved.

Looking at the potential risks for MIC within the ten DH sites in the survey, the following was observed:

- MIC seems to be connected to a low pH.
- Using sulphite as oxygen scavenger seems to increase the probability of MIC.
- MIC seems to be somewhat associated with a relatively low forward temperature.
- Using phosphate or ammonium as pH buffer seems to minimise the probability of MIC.
- The addition of hydrazine seems to limit biofouling and thus MIC.

2 Introduction

New insights in the corrosion mechanisms in Danish district heating systems has lead to a more detailed understanding. In 1995 an introductory survey regarding the presence of bacteria and localised corrosion was conducted in four Danish district heating plants. In addition, personnel at a large number of plants was interviewed about indirect indications of MIC (bad smell, slime, etc.). This survey provided indirect evidence of microbiological problems in a large number of the Danish plants.

As a reflection of these findings, one of the largest district heating plants in Denmark, the Metropolitan Copenhagen Heating Transmission Company (CTR), started to look for indicators of MIC in their more than 40 individual networks. The results were quite obvious showing that even though some of the networks were practically free of corrosion some were showing signs of both bacterial activity and localised corrosion. CTR has thus continued their effort to identify and mitigate MIC in their installations and has thus assured a longer lifetime for their investments.

At the moment microbiological data have been recorded for about 40 plants throughout Denmark. The number of bacterial cells within the water of these plants span from 10^2 to 10^6 cells/ml. The amount of cells within biofilms has been addressed in about 10 of the 40 plants ranging from 10^4 to 10^7 cells/cm^2. Within the same plants, general and localised corrosion rates have been measured. The general rate is generally relatively low between 2 and 30 micrometers per year, while the local rate may be significantly higher. Local rates of up to the range of mm/year have been measured.

Two major projects funded by the Danish Energy Authority under the Energy Research Programme has shed light on the mechanisms of MIC in district heating systems and the means of which the MIC may be handled. Parallel to the second Danish project, a project funded by the Nordic Industrial Fund, has worked on developing another unit for monitoring MIC in district heating systems.

Biofouling and MIC have conclusively been diagnosed in several Danish DH systems, including networks, boilers, and heat exchangers, even in systems utilising very high purity water. Consequently, MIC contributes a large proportion of the corrosion encountered in DH systems in Denmark. Information about the extent of biofouling and MIC in other countries is very limited. However, two reports (COST 511 project no. CH-3 and Microbiologica in CCP 1986/55 p.105) show MIC as important in Switzerland and Russia.

The aim of this project has been to address the significance and the consequences of biofouling and microbiologically influenced corrosion in the DH industry and to propose a method for MIC risk assessment. The outcome of this project will serve as guidelines for determining the necessary actions towards monitoring, mitigation and control of biofouling and MIC in the DH industry. It is further anticipated that the synergetic effect of bringing together microbiologists and corrosion engineers within the project group will foster new ideas for future development.

MIC has previously been addressed either from a microbiological or from a corrosion point of view. Arrays of corrosion methods have been assisted by a few simple biological measurements and vice versa. Both ways of handling MIC have resulted in a high degree of detail explaining mainly one side of the problem. The general corrosion rate, for example, measured either by weight loss or simple on-line methods (e.g. LPR), has traditionally been applied to technical systems. However, the methods are not likely to reveal localised corrosion, and biofilms may influence the measurements. The results of this project may reveal whether the traditional corrosion methods are applicable to MIC or not.

It is expected that combining forces having front line knowledge on materials, corrosion, and biofilms, will lead to the development of an array of efficient techniques for monitoring, mitigation and control of MIC in DH systems. Combining for example local in-situ molecular microbiological methods, as being developed at the Danish Technological Institute, with the available techniques for assessing local corrosion processes at the Swedish Corrosion Institute, it may be possible to achieve information on the relationship between local corrosion and distribution of bacterial strains. In other words it may be possible to see which bacteria causes local corrosion, and thus which specific bacterial strains are to be eliminated in order to prevent local corrosion.

2.1 Introduction to biofouling and MIC

This chapter covers an introduction to microbiology and corrosion. The two topics are initially treated separately and subsequently combined under microbiologically influenced corrosion (MIC). Furthermore, a short introduction to available analytical methods is given.

Microorganisms
Contrary to the larger complex organisms, we usually associate with life, microorganisms are single cell organisms that for the majority are so small that they cannot individually be observed by the human eye. The size of most bacteria lies around a few micrometer. Microorganisms, although they often look alike, may be very different in terms of their function. Microorganisms may cause diseases or even death but on the other hand, microorganisms handle essential functions, which we would rather not be without (e.g. the flora inside our intestines).

Metabolism
Microorganisms may utilise a wide range of energy sources and electron acceptors. Microorganisms are often categorised based on their source of energy. Energy may come from organic matter (as with humans), light (as with plants) or inorganic compounds. The associated bacteria groups are termed heterotrophs, phototrophs and lithotrophs respectively. For bacteria to be able to utilise the energy source, they need an electron acceptor. This electron acceptor is reduced while the energy source is oxidised and energy is released. The electron acceptor may be e.g. oxygen (utilised by aerobic bacteria), nitrate or nitrite (denitrifying bacteria), sulphate (sulphate reducing bacteria), various iron compounds (iron reducing bacteria) or organic matter (fermenting bacteria). The energy source and electron acceptor may be combined in any way yielding a wide variety regarding the metabolism of bacteria.

Apart from the use of energy to keep up the metabolism, the cells also need various compounds (e.g. carbon) to build new cell material. Again, the cells may be categorised based on e.g. their carbon source. Bacteria that can utilise atmospheric carbon, CO_2, like plants are termed autotrophic. Bacteria that can utilise organic bound carbon are termed heterotrophic. Thus, autotrophic bacteria are independent of the abundance of organic bound organic matter within their environment, while heterotrophic bacteria all need some source of organic carbon.

Taking a closer look at the heterotrophic bacteria, the types of organic matter that they are able to utilise and incorporate vary.

Some species can grow on many different compounds, while others are very specific in their choice of carbon source. Some of the more specific ones have e.g. specialised in degrading man-made toxic compounds.

These metabolic differences may be used to identify various groups of bacteria in an unknown sample. A rather new technique (Kjellerup et al., 2004) called microautoradiography (MAR) makes use of the cell metabolism in the way that the unknown cells are exposed to a specific source of carbon (e.g. acetate) which includes a radioactive isotope. All cells that utilise that particular substrate then become radioactive.

Other specific methods use the cell DNA/RNA which contains information about all the cell functions to identify single bacterial species or groups of bacteria (FISH) (Kjellerup et al., 2003).

Information obtained through such specific analysis may be used to describe possible corrosion mechanisms where bacteria are suspected to influence the corrosion. The information may also lead to specific mitigation strategies based on eliminating the type of energy or carbon source that the trouble causing bacteria utilise.

Biofilm
The majority of the world's population of bacteria do not live individually suspended in water, but are instead immobilised on all sorts of surfaces. It has been stated that 95% of all bacteria live immobilised on surfaces in biofilms (Characklis and Marshall, 1989). Why do these bacteria choose to live on surfaces? The answer is not unambiguous, but should be found within a range of advantages that the cell encounters in a biofilm (Flemming and Schaule, 1996)

- Different bacterial groups may benefit from each others functions (symbiosis). Strict anaerobic bacteria may for example be able to survive in an aerated environment if they are situated deep inside a biofilm where they are protected through the oxygen consumption by the above layers of aerobic bacteria. Different physiological groups may also utilise each others waste products as nutrition when they are situated close together in a biofilm.

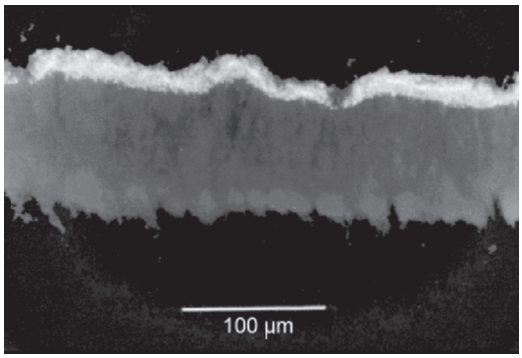


Figure 2.1. Cross section of a biofilm (http://www.erc.montana.edu/CBEssentials-SW/research/Control/kd-xu-image-caption.htm).

- Inside a biofilm cells are better protected against changes in the surrounding environment. This goes for chemical as well as thermal and physical changes. It is generally easier to kill a planktonic cell than it is to kill a cell that lives within a biofilm.
- Cells within a biofilm may communicate with each other through chemical signals and thus collectively respond to changes in the surroundings.

Biofilm may be encountered in all environments where water occurs, e.g. in lake sediments, river shores, and even inside industrial water bearing installations. Within natural systems biofilms may for example exist as a greasy slippery layer on rocks at the seashore. In industrial systems biofilms of such magnitude are seldom (with a few exceptions) encountered. In the pulp and paper industry and within the waste water treatment industry, biofilms may reach such thicknesses that their presence is obvious. It is, however, likely that biofilms may be found on every surface that is or has been in contact with water. Therefore, it is quite naturally that biofilm may exist on the inner surfaces of district heating installations.

Biofilm consists of a more or less dense layer of microorganisms. The thickness may vary from a few cell layers (a few micrometers) to several hundred micrometers; in extreme cases millimetres or centimetres. The biofilm thickness depends on a number of physical and chemical parameters like the availability of nutrients, the temperature, and the flow velocity. In district heating systems biofilms of up to 30 micrometers have been observed on stainless steel. On mild steel biofilms of several hundred micrometers have been observed.

A biofilm is generally characterised by (Flemming, 1991):

- High water content (approx. 70-95 %)
- High content of organic matter (approx. 50-90 % of dry matter)
- Large number of cells (10-90 % of organic matter)
- High content of proteins and carbohydrates

Microbiological analyses

Traditionally, analytical methods for quantitative and qualitative characterisation of microbiological samples have been based on growth within synthetic media. For example cells are counted by spreading them onto a solidified growth medium, incubating them for a number of days, and counting the number of visible colonies on the surface. Using different growth media and different incubation conditions the type of bacteria may be narrowed down to a group of bacteria.

The procedure is rather simple but quite time consuming, particularly if the type needs to be identified.

Recent findings have, however, shown that these traditional growth methods only find a small fraction of the total number of cells within the sample (Wagner and Amann, 1997; Amann et al., 1995).

By adjusting the concentration of the nutrient media to match the original habitat of the bacteria, the method may be slightly improved. However, this may increase the time for each analysis even more because the cells grow very slowly. The result of such tests often awaits for weeks or months (testing for sulphate reducing bacteria by growth methods within this project took four weeks).

Another drawback by using the traditional growth methods for qualitative measurements is that the quantitative distribution among different species is lost in the growth step. This may be solved by making serial dilutions for each type of medium, heavily increasing the amount of work needed for the analysis. The two methods mentioned above (MAR/FISH) solve this problem by introducing tests which act on a molecular level with either the cell RNA or the cell activity.

As an improved tool for cell counts, a method has been developed for counting the total number of bacteria (Kepner and Pratt, 1994). The sample is stained with a fluorescent dye that binds only to the cells, which can then be counted directly under a fluorescence microscope. By this method all intact cells, both the dead and the active, are counted.

Biofouling problems
Because the distribution of chemical compounds change with depth in a biofilm, the chemical properties at the surface of the underlying material may be totally different from the properties in the water. In natural waters containing oxygen, sulphate or nitrate and organic matter, one may therefore expect to see low pH values (as low as pH 2-3 has been reported) underneath relatively thick biofilms.

Due to this ability of biofilms to change the physical properties of a surface and the chemistry near it, they may create several problems in water bearing and wet technical systems. Furthermore, the mear physical presence of biofilm may in many cases cause problems on its own. Events of such unwanted biofilm formation are often referred to as “Biofouling”.

Problems caused by biofouling may reveal themselves in various ways, for example through:

- increased drag resistance within water bearing pipes increasing pumping costs
- clogging of filters, membranes, etc. decreasing efficacy
- increased and localised corrosion damage reducing lifetime of installations
- induced changes in water quality, e.g. production of hydrogen sulphide, which may cause corrosion and health risks
- low efficacy of disinfecting agents and risk of pathogenic (disease causing) bacteria residing in biofilms.

Many biofouling problems result in loss of system performance or system malfunction. This may be the case of increased cost for pumping, heat transfer, etc. Other problems may result in induced health risks for the people in direct contact with the system or the end users of produced products through product contamination. Other problems again, like microbiologically influenced corrosion, degrade the system irreversibly eventually leading to leakage, breakdown, etc. In such cases, removing the biofilm that caused the initial attacks will only slow down or stop the progressing reactions. It will not solve the already existing problems of e.g. decreased pipe wall thickness.

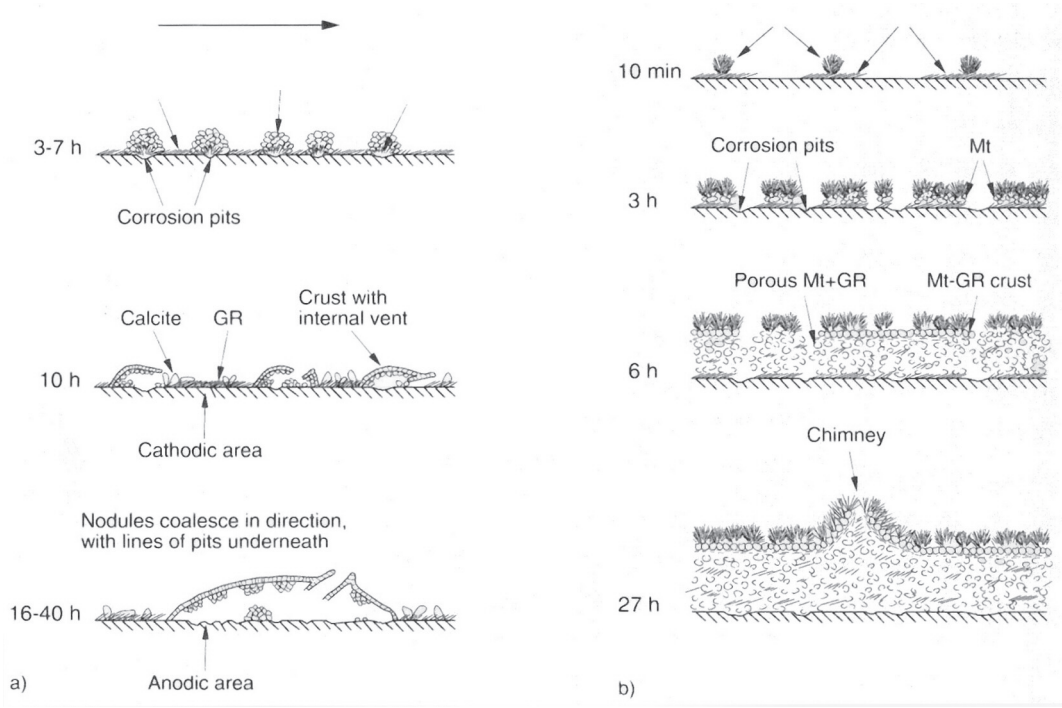
Corrosion
Biofilm may play an important role in the corrosion of metals. The main reason is that the cells within the biofilm, due to their metabolism, change the chemistry of the water around them. Since the basis for metallic corrosion depends highly on the water chemistry, it is obvious that a biofilm on the surface may alter the way the metal corrodes. Even in systems with otherwise welldefined water quality, like cooling and heating systems, biofilms can increase the corrosion to a point where the lifetime of the installation is significantly decreased.

Traditional corrosion
Mild steel and other active metals/alloys
Under circumstances without interference from bacteria, it may be assumed that active metals like mild steel will corrode when exposed to an aerated wet environment. It may also be assumed that the corrosion takes place with the same rate all over the wetted surface.

The corrosion process is often divided into an anodic process (actual dissolution of the metal) and a cathodic process (a process that gets rid of excess electrons). Usually, the corrosion rate is determined by the rate of the cathodic reaction. Thus, it is often this half of the corrosion process that is most interesting. If the environment contains oxygen, the reduction of oxygen will be the dominant cathodic reaction that consumes the excess electrons from the anodic dissolution of the metal. If oxygen is not present, other reactions will take over the cathodic reaction. This could for example be formation of hydrogen gas from water, reduction of metal ions or reduction of other organic or inorganic substances.

Corrosion of iron with reduction of oxygen as the cathodic reaction is outlined below as an example of a simple corrosion process without influence of microorganisms. Corrosion using oxygen as the cathodic reactant or oxygen corrosion may turn out different depending on the concentration of oxygen in the water. Figure 2.2 shows the principle development during corrosion of iron at two different oxygen concentrations.

Figure 2.2 Development of corrosion and corrosion products on iron at 50 °C during a) low oxygen content 0,44 mg/l and b) high oxygen content 3 mg/l (Smith & McEnaney, 1979).



At a relatively low concentration of oxygen, corrosion will attack the metal surface uneven and slowly grow to cover larger and larger areas of the surface. This type of corrosion normally affects only the uppermost layers of the metal. It does not create deep pits. The deposits of corrosion products will consist predominantly of magnetite (around the anodic sites) and green rust (around the cathodic sites).

At higher oxygen concentrations, the corrosion will start as local attacks, but spread relatively fast to cover the entire surface. The uppermost layers of the corrosion products formed will consist of the reddish lepidocrocite (γ FeOOH). Underneath a layer of magnetite/green rust will grow steadily in thickness. The distribution among magnetite and green rust will among other parameters depend on the pH at the surface of the metal.

In district heating systems in general, corrosion is minimised by removing as much oxygen as possible and by increasing the pH. The Danish district heating Association prescribes a pH between 9.6 and 10.0 in order to prevent corrosion. It is usually practically impossible to remove all traces of oxygen from the water before it is fed to the system, although effective degassers can bring the concentration down to the lower ppb (parts per billion) level. The remaining oxygen will at a suitably high pH be incorporated in a protective magnetite film that forms on the metal surface and protects against further corrosion. If the oxygen influx to the system can be kept at a minimum and the pH is stable between 9.6 and 10.0 the system will be sufficiently protected against further corrosion; at least in the case where there is no interference from bacteria growing on the surface.

Unfortunately, the real situation is not always so perfect. Quite often atmospheric air will be added to the system during routine maintenance and repairs. Addition of air will among other effects cause the pH to drop. In the worst case the pH drop will create instability within the magnetite film so it no longer is protecting the underlying surface. However, if the pH is brought back up, the film will regenerate again. After several oscillations of oxygen content and pH, the magnetite film will grow in thickness and porosity. This will result in a film that is less protective and furthermore a good basis for housing a biofilm.

Stainless steel and other passive alloys
Under ”sterile” conditions, one may usually assume that passive alloys like stainless steel and to some extent copper do not corrode in relatively neutral aqueous environments. The chemical composition of the alloy causes formation of a passive film on the surface. On stainless steel this film will form already when the steel is exposed to humid air.

When passive metals corrode, the attacks will thus be of a local nature in terms of pitting or

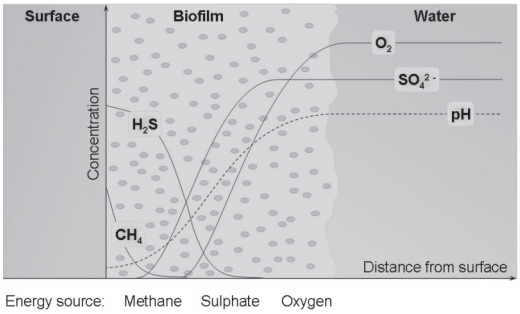


Figure 2.3 Different processes caused by different bacterial groups inside a biofilm may create local chemical environments that are totally different from the bulk water outside. In this thought example, oxygen is consumed within the outmost layers of the biofilm. In the layers beneath the oxygen has been depleted and other biological processes like the reduction of sulphate or the production of methane take over. The processes result in production of sulphide and a much lower pH inside the biofilm than outside (Trostmann et al., 2001).

crevice corrosion. If there is sufficient cathodic activity to drive the anodic dissolution of metal within the pit/crevice, the attack may grow deeper into the surface and continue to do so until the material is penetrated. It is needless to state that the effect of such corrosion within a hot district heating environment may be devastating.

Finally there are metals and alloys that are very active and could be expected to corrode rapidly, but do not do so. That goes particularly for aluminium which forms corrosion products that are so dense and stable that they protect the base metal against any further corrosion. The same may be true for iron and mild steel under ideal district heating conditions (no oxygen and high pH).

If parts of the metal surface for some reason is isolated from the surrounding bulk water, local environments may be created that are far more corrosive than the bulk. This may for example be the case in crevices between flanges, underneath seals or between heat exchanger plates. Such an accelerated corrosion attack is termed crevice corrosion. The chemistry within the crevice may be very far from the chemistry outside, mainly due to the limited transport of ions to and from the crevice. The water exchange within the crevice is negligible and the exchange of ions is thus based solely on diffusion.

A similar situation may occur if the surface is covered by deposits or debris. In district heating systems this may be most predominant within storage tanks and other installations where the water flow is low. This particular type of corrosion is termed “under deposit corrosion” though the basic phenomenon is the same as for crevice corrosion.

For both crevice and under deposit corrosion there needs to be a process that initiates the corrosion. When the corrosion processes are initiated they will accelerate the corrosion rate by changing the local chemistry. One factor that may trigger the initiation could be the activity of microorganisms growing on the surface.

Effect of microbiology on corrosion

As long as “sterile” conditions exist, corrosion processes are normally quite predictable. They follow certain rules depending on the chemistry of the water, the temperature, etc. When the system is influenced by bacteria, the situation may, however, be totally different. Not only can bacteria change the chemistry within the water in terms of organic matter and inorganic salts, they will also, if they grow on the surface, alter the chemistry near the surface (figure 2.3). Therefore, the result of a biofilm will be that there is no longer a direct connection between the chemistry measured within the bulk water and the corrosion behaviour of the metals in the system. Even though the majority of the

Figure 2.4 Pitting within a heat storage tank within a district heating facility in Denmark. The corrosion is started underneath a thick layer of sludge composed of corrosion products, organic matter and a high number of bacteria.

biofilm consists of water, the cells within it can consume or produce chemical substances at a rate so fast that the concentrations inside the biofilm due to diffusion limitation will become different than in the bulk water outside.

As the corrosion of metals is often determined by the water chemistry, the chemical alterations created by a biofilm on the surface of a metal will most certainly change the prerequisite for corrosion. How fundamental the changes are depends on the nature of the metal and the magnitude of the chemical changes. The biological activity may change the rate of an already ongoing corrosion or it may initiate corrosion where there was no corrosion before.

No matter which type of corrosion enhancement the biofilm creates, the overall result

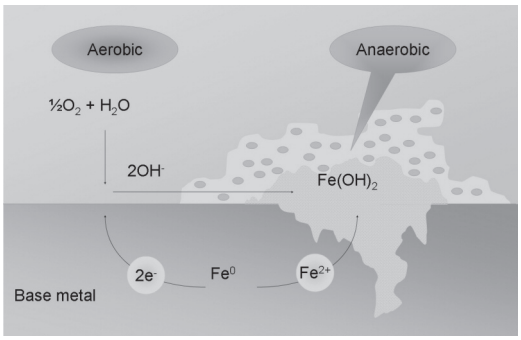


Figure 2.5 Biofilm causing localisation of anodic sites. The biofilm may further increase the corrosion rate by changing the chemistry inside the formed corrosion pit (Trostmann et al., 2001).

will be a reduction of the system lifetime and possibly increased risk for the people exposed to it. The greater risk occurs when the corrosion takes place as pitting or crevice corrosion. In such cases even thick metal constructions may be penetrated within short time.

Different actions of MIC

Given the complexity that often characterises MIC, there are no certified methods of detecting MIC. The literature reports a wide variety of MIC cases where all facts point towards influence of bacteria. A number of models for the interactions between bacteria and metals have been proposed and some of them have even been proven in laboratory tests. In general, it may be assumed that any biological process that takes place on a metal surface will have some influence on the corrosion of that metal (Borenstein, 1994).

The following examples are among the more frequently reported:

Oxygen depletion

The fact that a biofilm in an aerated environment will use oxygen and therefore cause the oxygen concentration underneath it to drop may be the sole reason for the initiation of localised corrosion. The area underneath the biofilm will be favoured as the anodic site whereas the surrounding area will act as cathode (Figure 2.5).

Cathodic depolarisation

Under anaerobic conditions, production of hydrogen gas is a possible cathodic process that under the right circumstances may drive a corrosion process. The production of hydrogen gas is often limited by the diffusion of hydrogen away from the cathodic areas on the surface. Some bacteria are capable of taking up hydrogen in their metabolism. This goes for e.g. methanogenic bacteria that convert hydrogen and carbon dioxide to methane and water. These bacteria may increase the maximum rate of the cathodic reaction, being production of hydrogen, by continuously removing hydrogen from the surface. It may be speculated that the interaction of bacteria and cathode process in fact is a synergy where the population of e.g. methanogenic bacteria becomes most dominant around the cathodic sites due to the abundance of hydrogen and thus increase the corrosion rate.

Production of hydrogen

On the other hand there are bacterial groups that produce hydrogen gas. These may cause another form of corrosion called hydrogen embrittlement. Hydrogen can penetrate almost any material including most metals to some extent. If the metal contains hollow voids, the hydrogen may be concentrated inside these voids. The pressure of hydrogen inside the voids may increase to such an extent that the metal is pushed apart in flakes. This type of corrosion may occur in district heating systems. However, there are no reported cases yet.

Acid production

Many bacteria produce acids as a by-product of their metabolism. It could for example be carbonic acid (the end product for most aerobic and some fermentative processes), organic acids like acetic acid or even sulphuric acid (from biological oxidation of sulphide). These processes will obviously lower the local pH value. In district heating systems it is not unlikely that a thin biofilm may lower the pH from 9.6-10 to 8 or 7. Measurements of local pH inside a corrosion pit from a Danish district heating facility have shown pH values as low as 5. Even a drop to pH 7 would cause the magnetite film to become unstable.

Production of sulphide

The sulphate reducing bacteria that are capable of reducing oxidised sulphur compounds like sulphate, sulphite and thiosulphate to sulphide are usually obligate anaerobic. Thus, they are not able to grow in an aerated environment. Nevertheless, there are a few species that can manage to maintain a stable metabolism at low oxygen concentrations, but they cannot reproduce unless they are in an anaerobic environment (Wieringa et al., 2000).

Some of the SRB's are thermotolerant or thermophilic, meaning that they either can or prefer to grow at elevated temperatures. In district heating systems, all prerequisites for growth of sulphate reducing bacteria are fulfilled, and

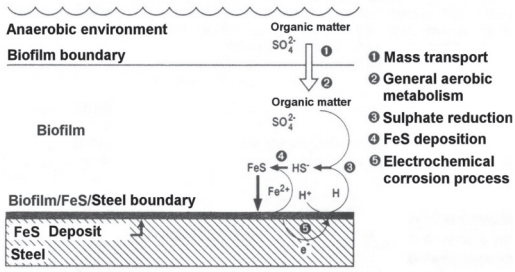


Figure 2.6 Processes of SRB corrosion of mild steel under a biofilm in an anaerobic environment. (Lee et al., 1995).

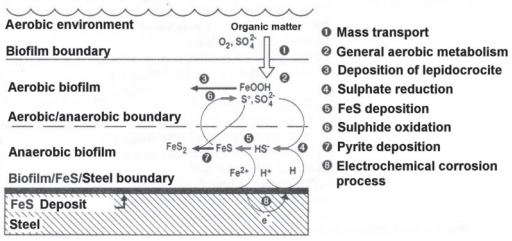


Figure 2.7 Processes of SRB corrosion of mild steel under a biofilm in an aerobic environment. (Lee et al., 1995).

some presence of this bacterial group may thus be expected.

The influence of SRB on corrosion covers e.g. cathodic depolarisation (by hydrogen consumption at the cathode – most significant at low pH), anodic depolarisation (by the formation of iron sulphides), production of corrosive iron sulphides (that catalyse the cathodic production of hydrogen) or sulphide induced cracking. The effect of SRB on both the cathodic and the anodic reactions are illustrated in figure 2.6.

If the SRB grows in a biofilm with the bulk water outside being oxygenated, a cyclic reaction of iron sulphides may initiate and continue to run even after the external source of sulphur has been used up (marked with red arrows in figure 2.7). A similar process may take place if the oxygen concentration in the bulk water fluctuates.

Under both aerobic and anaerobic conditions, SRB activity may result in formation of sulphide containing deposits on the surface of the steel. Anaerobic conditions will create mainly iron sulphide (FeS), mackinawite (Fe_9S_8). Aerobic or alternating aerobic/anaerobic conditions may continue the processes to elemental sulphur and pyrite (FeS_2), (marked by blue arrows in figure 2.7).

Both deposit types and in particular pyrite acts corrosive by catalysing the cathodic production of hydrogen. Thus, they speed up the corrosion processes compared to the corrosion as it would take place in the bulk water. Neither mackinawite or pyrite take actually part in the corrosion process, and they may therefore continue to raise the corrosion rate once they are formed.

Therefore, if MIC caused by SRB has been identified it is not enough to kill off all the bacteria. The elevated corrosion rate may continue as long as the corrosive deposits are still in the system. It is also important to notice that an attempt to remove the deposits by acidification of the system will increase the cathodic activity even more (by lowering the pH more hydrogen ions are available for production of hydrogen gas).

One may have to accept an increased corrosion rate during cleaning.

Deposition of cathodic active compounds
Manganese oxidising bacteria are capable of depositing manganese dioxide (figure 2.8) which is known as a powerful cathodic reactant. For the same reason manganese dioxide is widely used in the battery industry. If manganese dioxide is deposited on the surface of stainless steel, a potential difference of several hundred millivolt may be created between areas with deposits and areas without. This potential difference may be sufficient to initiate corrosion in environments where stainless steel would be otherwise passive. The effect on mild steel types have been shown not to be serious since the electrical connection between the steel and the manganese dioxide is disconnected by the production of corrosion products in between.

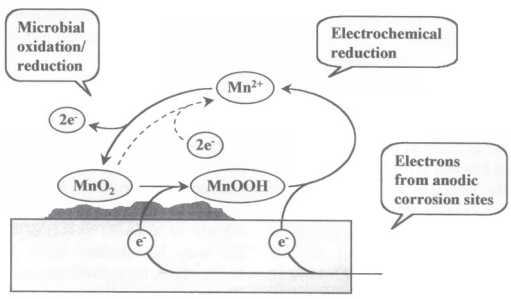


Figure 2.8 Bacterial oxidation of manganese may work as a cathodic reaction in corrosion (Olesen, 1998).

Summing MIC processes
The above mentioned biological processes along with the bacterial groups usually responsible for them are listed in table 2.1. The effect on cathode and anode processes are also given.

Available methods for measuring and monitoring MIC

In order to gain access to the inner surfaces in a district heating system, it is necessary to empty the system and perform manual inspection. This would cause severe oxidation of the passive oxide films inside the system and may create a situation regarding corrosion that is worse than prior to the inspection.

In order to minimise the manual inspection, it is possible to install test surfaces that can be taken out and evaluated on a regular basis. The test surfaces may be inserted individually through examination ports or valves, or they may be exposed in a side stream. An advantage of the latter option is that the entire side stream may be depressurised prior to extracting test surfaces to maximise the safety of the operation. Figure 2.9 shows a schematic illustration of a side stream exposure unit that allows for exposure of several surfaces under a simulated pipe flow. Figure 2.10 show examples of exposed surfaces.

Exposed surface samples may be analysed for corrosion as well as deposits. General corrosion rates may be measured by weight loss. Local corrosion rates may be measured by e.g. laser-interferometry, which gives the topography of individual pits. Figure 2.11 shows examples of such topographical measurements.

Table 2.1 Biological processes that may influence corrosion in district heating systems

	Bacterial group	Cathodic effect	Anodic effect
Oxygen gradients	all aerobic bacteria	localisation of anode and cathode	
Cathodic depolarisation	e.g. metahanogenic bacteria and SRB	depolarisation through consumption of hydrogen	
Production of hydrogen gas	e.g. certain fermenting bacteria	hydrogen embrittlement	
Production of acid	most fermenting and anaerobic bacteria	increase production of hydrogen	disabled the formation of passivating magnetite
Production of sulphide	Sulphate reducing bacteria	increase production of hydrogen by consumption or catalysis	increase the dissolution of iron by formation of FeS
Production of cathodic active deposits	e.g. manganese reducing bacteria	creates a powerful cathode	

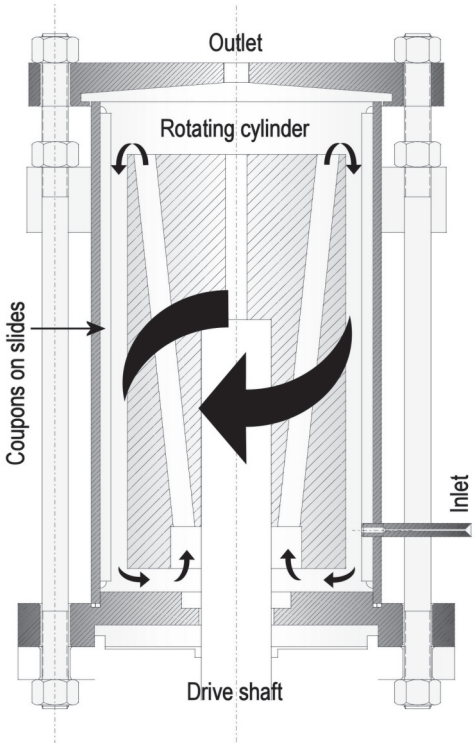


Figure 2.9 Cross section of an exposure unit showing principle of operation.

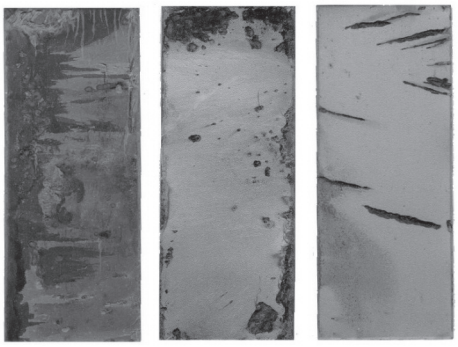


Figure 2.10 (left) Test surfaces after exposure in a district heating system

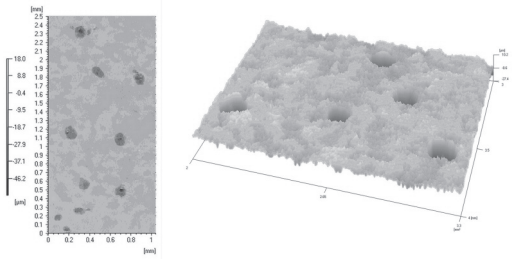


Figure 2.11 (right) 2D and 3D topographic representation of local corrosion attacks on mild steel (Dark colours represent deep areas).

2.2 Case story: Heat station, Frederiksberg

This case story describes the process of detecting, mitigating and preventing MIC in the heat station in Frederiksberg, Copenhagen (FVC).

The heat station FVC was taken into use in 1996 as a peak load boiler station supplying heat to the greater Copenhagen district heating network (owned and run by the Metropolitan Copenhagen Heating Transmission Company, CTR). In 1999 severe corrosion damages including MIC were detected within the system. The main cause for this was thought to be insufficient cleaning prior to use combined with the low number of heat supply hours.

MIC within the heat station was mitigated by:

Mechanical and chemical cleaning.
Changes in construction details.
Changes in maintenance procedures.

These initiatives have caused a significant reduction in the observed corrosion rates (figure 2.12)

Continuous monitoring of corrosion has shown that contamination by oxygen has caused the corrosion rates to remain high from fall 2001 to spring 2002.

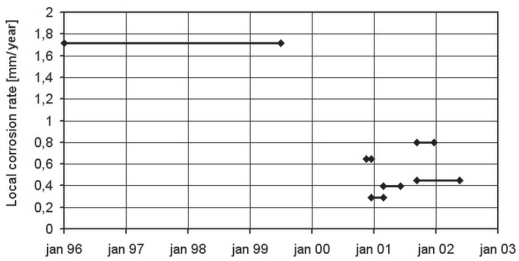


Figure 2.12. Local corrosion rates for carbon steel within FVC. The rate for the period 1996-1999 is estimated based on through wall pitting of a drainpipe, while the rest of the rates are measured on carbon steel test coupons exposed in a rotating cylinder unit

History

The heat station at Frederiksberg is one out of 18 peak load boiler stations within the supply area of CTR. The station delivers heat to the CTR transmission network in peak load situations. FVC was established in 1995 with two 50MW boilers and two 50MW heat exchangers and was taken into use primo 1996. In 1999 the station was expanded with an additional two boilers. Thus, the maximum load is now 200MW. At the same time a third heat exchanger was installed and the two old ones were modified to meet the higher maximum load. The total water filled volume of the station is today around 250 m^3. Original fill water and routine supply water is taken from the transmission network.

The plant has only a limited number of heat supply hours each year (100-1,000 hours/year). Inbetween supply, the temperature throughout the plant is kept up by exchanged heat from the transmission network (separate heat exchanger). The temperature during off hours is set at 80°C and the flow to 74 m^3/hour. During heat supply from FVC the flow rate is significantly higher (figure 2.13).

Since the plant was taken into use, a monitoring programme for water quality has been running. Each month water samples are taken and analysed for a range of chemical parameters (table 2.1).

Table 2.2 Water quality parameters and limits for FVC.

Parameter	Unit	Limit
pH	---	9.3-10.0
Conductivity	µS/cm	< 15
Acidic conductivity	µS/cm	< 1
Oxygen	ppb	< 100
Hardness	dH	< 0,0
Fluoride	ppm	< 0,5
Chloride	ppm	< 1,0
Suspended solids	ppm	< 10,0
Looks	---	Clear

From 1996 to 1999 no noteworthy operational problems have been encountered. However, on several occasions a bad odour of hydrogen sulphide (rotten eggs) from the water was encountered. Each time the water was replaced with fresh water from the transmission system.

Water quality data from the period 1996-1999 are shown in figure 2.14 and 2.15. Each time the water has been replaced due to bad odour, a drop in conductivity can be observed. The concentration of organic matter (measured as potassium permanganate value), however, increased rapidly following each water replacement and dropped slowly during the following months.

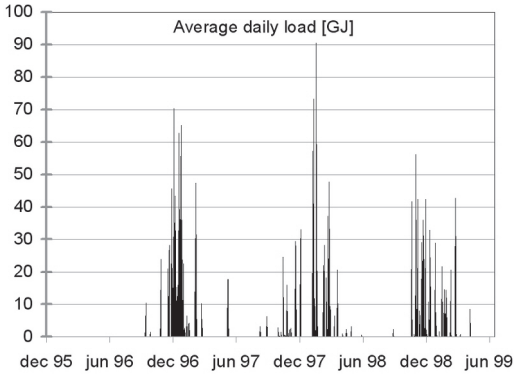
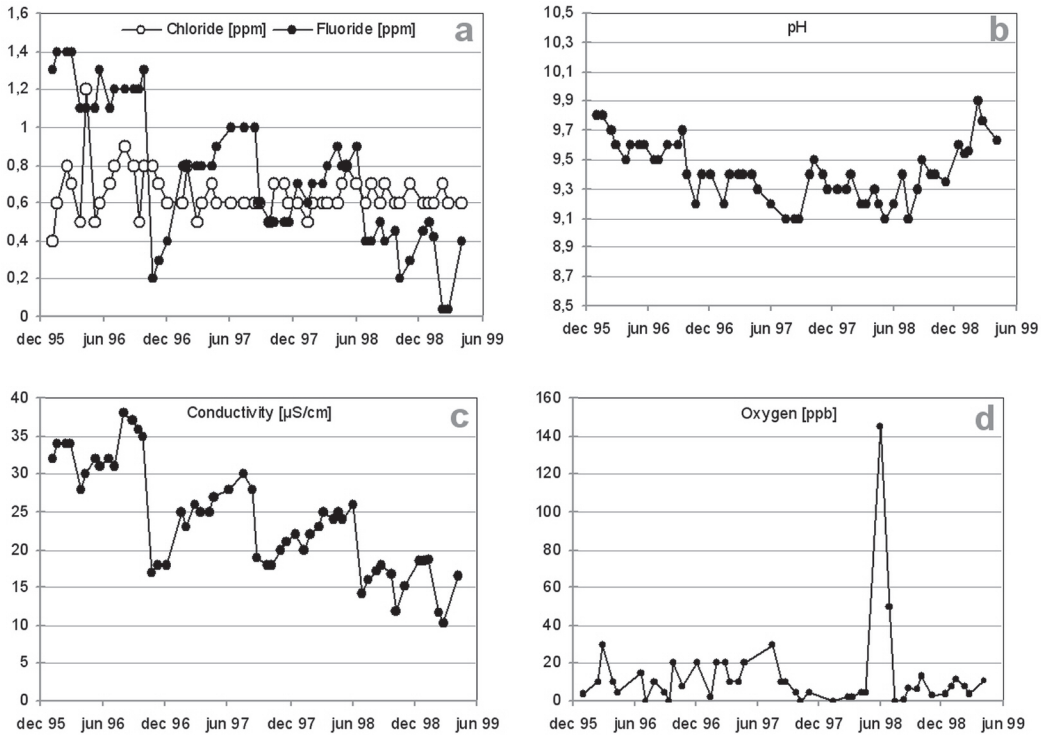


Figure 2.13. Heat supply pattern for the heat station.

Figure 2.14. Water quality data from 1996 to 1999.



Even though the water quality limits have been exceeded a few times, the situation in general does not imply any significant corrosion going on. Nevertheless, during 1999 a number of severe corrosion damages were encountered within the plant.

Observed corrosion damages

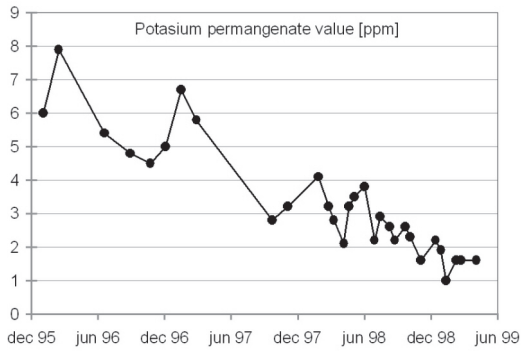
In the spring of 1999 two leaking heat exchangers at FVC were inspected. The main reason for the leaks was determined to be defects in the rubber gaskets between the plates. A large amount of sludge in the bottom region of the heat exchangers was however analysed and it turned out that the sludge contained a large number of bacteria (even SRB) along with a high concentration of organic matter. During a detailed inspection of the heat exchanger plates through wall pitting was observed on a few plates.

These findings lead to further inspection of the entire plant in order to establish a reason for the corrosion found in the heat exchangers and to find out if there were other parts that were similarly corroded.

Examining the transmission side of the heat exchanger plates did not show any indications of corrosion. Scattered grease spots were seen, but no biofilm could be found within these spots.

On the boiler side of the heat exchanger plates, a black porous deposit was covering the entire surface. Around points where the plates had touched, a more sturdy and dense type of deposit could be observed. At a few points actual corrosion products were found. Underneath the dense black deposit the surface was corroded in form of pitting. Figure 2.16 shows a profile of one of these pits. This particular pit was measured to be about 50 microns deep and about 300 microns in diameter.

Figure 2.15. Concentration of organic matter given as potassium permanganate value from 1996 to 1999.



Based on the findings from the corroded heat exchanger, a detailed investigation of the remaining system was initiated.
Particularly advanced corrosion was found within the drainpipes from the four boilers. In a few cases the corrosion had penetrated welds

Figure 2.16 Profile of a pit located underneath a dense black deposit on the boiler side of a AISI316 heat exchanger plate.

causing minor leaks into the insulation material and corrosion on the outside of the pipes. On the inside of the drainpipes, several tubercles were found. In some cases the tubercles had spread downwards in a fan shaped pattern. The pits underneath the tubercles were measured to be in the range of several hundred microns in depth (figure 2.17).

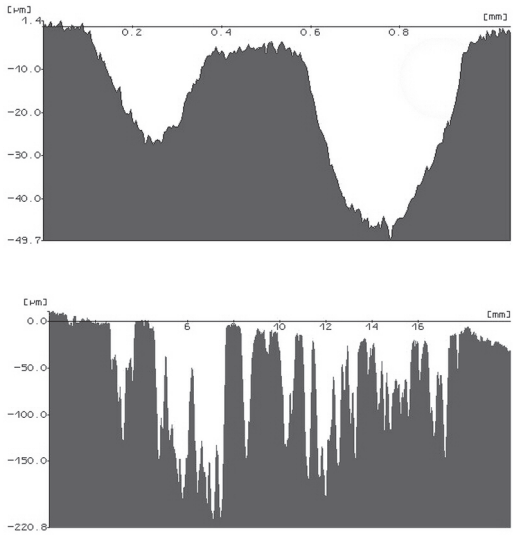


Figure 2.17. Profile of pits on the inside of a boiler drainpipe

Expected versus observed corrosion

Based on the water quality data collected in the period 1996-1999 no significant corrosion was expected on any of the materials used in the system. Nevertheless, through wall pitting of AISI316 stainless steel heat exchanger plates (0.8 mm) and carbon steel welds (6 mm) were observed along with scattered tubercles and pits on both materials. Since the water chemistry cannot explain the observed corrosion, the cause must be found elsewhere. Thus, the attention was turned towards MIC and a series of analyses dealing with MIC relevant parameters were carried out.

Following the commencement of the system in 1996, bad odours of hydrogen sulphide were encountered occasionally. Apart from these observations, however, no actual measurements of sulphide were made. During the investigation of the corroded heat exchanger in 1999 the following was found:

- Large number of bacteria
- Large amounts of organic matter
- Sulphide
- Particularly corrosive bacteria (SRB)

Furthermore, it was pointed out that corrosion products from the corroded drainpipes contained a large number of bacteria, and that the local concentrations of bacteria were somehow related to the localised corrosion attacks (figure 2.18). Examination of the corrosion attacks and the corrosion products showed that oxygen had only played a minor part during the corrosion process.

These observations lead to the conclusion that the corrosion that had taken place in the district heating plant was primarily a product of microbiologically influenced corrosion (MIC), possibly through the action of sulphate reducing bacteria (SRB).

The basic cause to MIC taking place is assumed to be an unfortunate combination of the lack of sufficient cleaning during establishing and prior to start-up and the unfortunate operation scheme with few heat supply hours. This combination implies all the conditions for uncontrolled growth of microorganisms within the system.

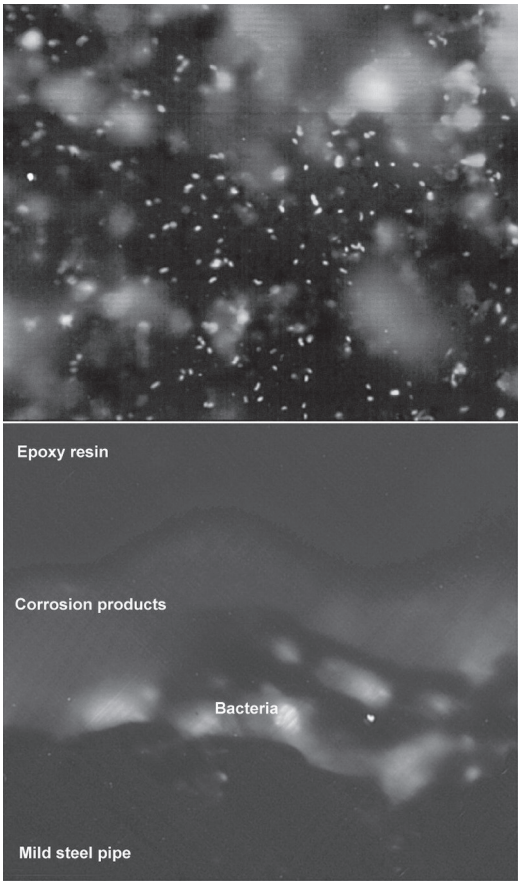


Figure 2.18. Top: Bacterial cells in corrosion products. Bottom: Bacterial cells under the corrosion products of a tubercle.

System cleaning
Following the identification and distribution of MIC, a series of activities were carried out in order to stop the ongoing corrosion attacks and to prevent further corrosion:

- Replacement of heat exchanger plates
- Replacement of drainpipes
- High pressure cleaning of boilers
- Fog-disinfection of pressure tank
- Changes of pipe layout to minimise deposit
- Repositioning of the side stream filtration to maximise particle removal
- Chemical (alkaline) cleaning of boilers
- Chemical (acidic) cleaning of heat exchangers

Prior to cleaning the water contained around 10^5-10^6 bacterial cells per ml. During the mechanical cleaning about 50 kg dry matter (hereof 14 kg organic matter) was removed based on analysis of the effluent. After cleaning the bacterial content was lowered to 10^3 bacterial cells per ml corresponding to a 100-1,000 fold reduction.

Following the cleaning of the system, the operating personnel have continued to pursue the sources for bacterial growth by implementing the following procedures in their daily work:

Flushing drainpipes
In fall 2000 the boiler drainpipes already contained sludge/debris again. Therefore, the operating personnel was asked to flush all drainpipes until clear water appeared and to do this on a regular basis. During the first weeks the water was black and smelly when the valves were opened, but as time progressed the draining time to get clean water decreased. At the moment the plant personnel have epitomised the drainage so they obtain a high flush rate for a short period of time and they have established a standard procedure of flushing the system twice every week.

In the summer 2001 the water flushed from the drainpipes had a concentration of organic matter around 6 ppm (given as carbon). During regular drainage make up water from the transmission system containing around 0.5 ppm organic carbon was added. The concentration of organic matter within the system should therefore be cut in half every five months solely based on dilution. Measured values of carbon content shows a similar development (figure 2.19). The content does, however, stabilise around 2-3 ppm carbon.

Filtration
A side stream filtration is placed at the lowest point in the system just before the heat exchangers. The filter contains a number of 5 micron PA cartridge filters and two magnetic rods to remove suspended magnetite particles. The filter is only activated when one or more boilers are operated (typically 10% of the time).

The filter was moved from a previous location on the first floor in the boiler room, where it was fed with water from the main flow from the boilers. In its new location the possibility of feeding the filter with particulate matter has improved.

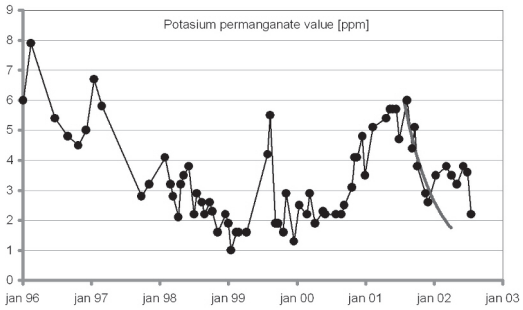


Figure 2.19 Dilution of carbon content through drainage. Red: theoretical development, Blue: measured.

Water samples were taken from a drainpipe of one of the boilers during regular flushing. One sample was filtered through a 0.22 micron filter before the organic content was analysed. The other sample was analysed unfiltered. The organic content in the two samples was almost identical (2.9 ad 2.8 mg/l), meaning that the 0.22 micron filter did not withhold any organic material from the water and that the majority of the organic materials thus is assumed to be dissolved.

In order to determine the effectiveness of the filter regarding removal of organic and inorganic materials, a number of samples were taken from the filter cartridges and the magnetic rods. These had been in use about one year, with about 950 hours of operation. In that period roughly 16,000 m^3 was pumped through the filter.

Analyses of the samples showed that about 1.4 kg of dry matter was withheld in the filter corresponding to a reduction in the entire system volume (250 m^3) of about 5.6 ppm. The organic content of the withheld material was only about

Figure 2.20. Picture taken from the inside of the flue gas cooler of one of the boilers. Notice the scales on the lower 5-10 cm of the wall surface.

2.5%, and the reduction of organic content is thus only assumed to have been about 0.1 ppm.

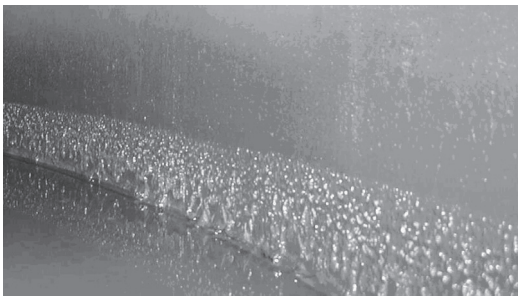
The filter seems to perform acceptable regarding removal of particulate matter. However, since organic matter within the system is in a dissolved form, the efficiency towards organic matter is very low.

Minimising boiler inspections
Every year the four boilers have been inspected after the water has been drained off. These inspections cause a massive amount of oxygen to enter the system and to oxidise all inner surfaces. The inspections are assumed to be the main reason for the remaining elevated corrosion rate due to oxygen corrosion. It has been stated that the number of inspections should be kept at a minimum and that the inspections may do more harm than good.

Changing pressure tanks
A previously installed pressurised tank (80 m^3) which has maintained a constant system pressure was replaced by four smaller tanks (2.2 m^3 each) with rubber membranes. This has reduced the amount of stagnant water significantly. Furthermore, a possible oxygen source from a nitrogen generator that fed the large tank has been eliminated.

Boiler changes
A closer look at the boiler construction revealed risk for deposit build-up. The flue gas cooler, consisting of cylindrical pipe heat exchanger with the gas flowing inside the tubes, is positioned vertically. This results in a relatively low upward flow of water inbetween the gas pipes. The bottom of the flue gas cooler thus experiences very little water movement, and it is therefore expected that particulate matter will settle here.

An investigation of the inner surfaces in the flue gas cooler revealed that the drain from the cooler was positioned about 5 cm above the bottom. Furthermore, it was found that particularly the lower 5-10 cm of the inner surface was covered by deposits under which localised corrosion had taken place (figure 2.20).



Corrosion attacks were evaluated by taking a cast of the surface of one of the gas pipes. The cast was measured using laser interferometry, revealing pits of up to 400 microns in depth. The actual depth is, however, expected to be larger since the cast showed signs of pinholes where the cast material had not penetrated completely.

The construction of the boilers has been altered so the drain from the flue gas cooler is now positioned lower. It has, however, not been possible to position the drain in the centre of the cooler. Thus some deposits may still be expected.

MIC monitoring
Since the cleaning of the system in 1999/2000 a monitoring programme, including scale and corrosion has been running. The following has been concluded at the moment:

- There is still a significant amount of bacterial cells in the system
- Production of sulphide occurs
- Severe oxygen corrosion takes place even though point measurements (every second or third month) of oxygen shows values under the limit.

The massive corrosion due to oxygen has made it impossible to evaluate other forms of corrosion. The corrosion products still contain a lot of bacteria, but the main reason for the corrosion is oxygen in the water.

Nevertheless, the corrosion rate has been lowered compared to the rates prior to the cleaning. Actions towards minimising pollution by oxygen and organic matter have thus worked to some extent.

3 International survey

In order to cover a representative part of the district heating plants within the IEA member countries, ten particular locations have been chosen. The criteria for choosing the locations have been representation of:

- Several member countries
- Several energy sources
- New and old plants
- Different water qualities
- Different water treatment strategies

Selected locations
The following locations have been selected:

- FŐTÁV Rt. – Budapest, Hungary
- TERMO Děčín, a.s. – Děčín, Czech Republic
- Hässelby - Stockholm, Sweden
- Värtan - Stockholm, Sweden
- Helsingin Energia – Helsinki, Finland
- Aarhus Kommunale Værker, Transmission network – Aarhus, Denmark
- Aarhus Kommunale Værker, Distribution network– Aarhus, Denmark
- Stadtwerke Lemgo GmbH – Lemgo, Germany
- Stadtwärme Lienz Produktions- und Vertriebs-GmbH – Lienz, Austria
- Southampton Geothermal – Southampton, United Kingdom

In the following a description of the locations will be given.

3.1 Selected district heating systems

Figure 3.1 Installation of monitoring equipment in Budapest.

FŐTÁV Rt. - Budapest, Hungary
The Budapest District Heating Works Co. Ltd. (FÕTÁV Rt.), founded in the 1960s, supplies heating energy for about 700-800,000 citizens in Budapest – about 1/3 of the city's population. The total subscribed heat capacity was in 1995 around 1,900 MW.

The monitoring equipment has been installed within the service area covered by the North-Pest plant. The sampling point is located within a substation, which delivers heat to a larger apartment building.

TERMO Děčín, a.s. Děčín, Czech Republic
The project of using geothermal energy in Děčín commenced in the early 1990s but had to wait a long time for a strong investor to emerge. Construction started in October 2000 and was completed in September 2002.

Energy in Děčín is "concealed" in a vast underground lake from which water with the temperature of 30 °C flows out through natural overpressure of 20 metres of a water column to the ground from the depth of 550 metres. The bore hole yield is 54 litres a second. By means of heat pumps, geothermal water is used for generating thermal energy. After cooling down to 10 °C and simple treatment, it meets requirements for quality drinking water and is supplied to the municipal water reservoir in the volume of approximately 1 million m^3 a year.

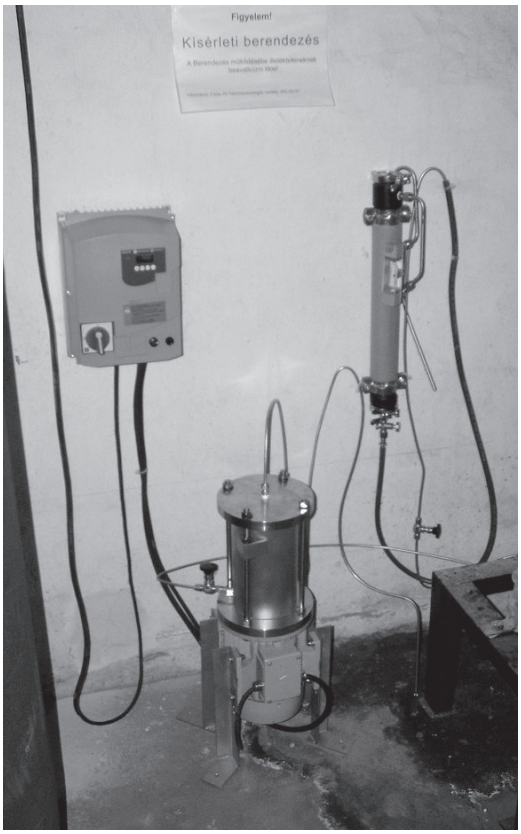
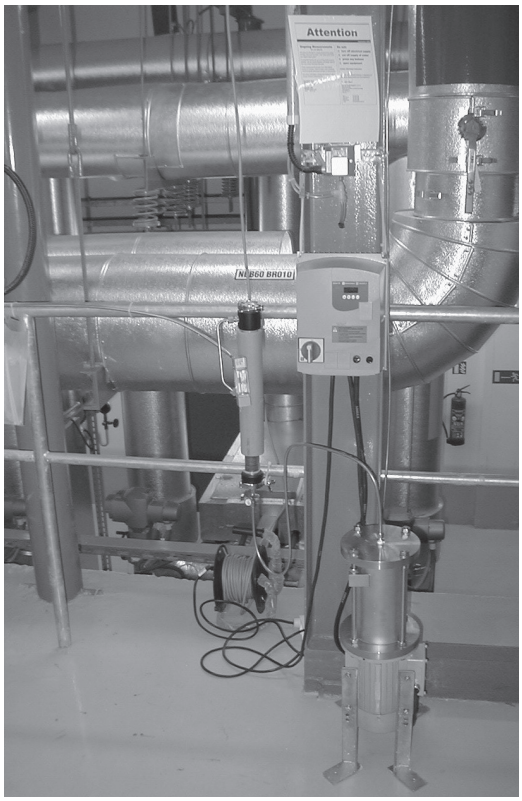


Figure 3.2 Installation of monitoring equipment in Děčín.



The water's passage from the bore hole is difficult to change, therefore the source is supplemented by a heat reservoir. The limited flexibility of using geothermal water from the bore hole also precludes intermittent operation of heat pumps and motors, as is otherwise common with CHP plants.

Network water of the return pipe with the temperature of approximately 55 °C is heated up by means of a heat pump system to a temperature of about 72 °C, subsequent further heating up to about 90 °C is ensured by the heating output of motors. Electricity generated through cogeneration primarily serves for driving the heat pump compressors and other circulation pumps of the source and the distribution network. If output above 9 MW is necessary, further heating up to a maximum of 110 °C and the remaining necessary output capacity is provided by peak boilers using natural gas.

Total annual heat supply from the source is approximately 280 TJ. One third of heat generation should be covered by geothermal heat. The source's total efficiency expressed as the share of heat supplied to distribution and the calorific

value of consumed natural gas in an annual aggregate ranges between 120 and 130%.

Extracted from a publication in: News at SEVEn, June 2004, Prague, SEVEn, The Energy Efficiency Center, o.p.s., www.svn.cz

The monitoring equipment in Děčín is installed within the heating plant using water from the cold return of the network.

Hässelby - Stockholm, Sweden
The major parts of the Hässelby network was built 22 years ago. However, smaller sections date back to 1951. Energy comes mainly from burning pellets. Oil and heat pumps are used as backup.

During the heating season, the water temperature ranges from 70-120 °C out of the plant to 35-60 °C in the return. Outside the heating season, the temperature ranges from 80-90 °C to 40-45 °C. The total volume of the network is 32,000 m^3.

The plant uses deionised water. The water is ion exchanged and filtered through mixed bed filters. In the early years raw water was used. Feed water changed from softened to deionised in the 70s. Feed water is deaerated thermally. Water analysis covering: pH, conductivity, fluoride and calcium is performed every other week. The rate of water exchange per year is estimated to be 50-100%.

According to the Swedish Corrosion Institute, which has been responsible for all communication to and from the Hässelby plant, the plant has no recent history of corrosion problems besides a few cases of external corrosion.

The monitoring equipment is installed at the cold return at the heating plant.

Värtan - Stockholm, Sweden
The major parts of the Värtan network was built 23 years ago. However, smaller sections date back to 1961. Energy comes mainly from burning coal. Heat pumps and oil are used as backup.

During the heating season, the water temperature ranges from 70-120 °C out of the plant to 35-60 °C in the return. Outside the heating season, the temperature ranges from 80-90 °C to 40-45 °C. The total volume of the network is 90,000 m^3.

The plant uses deionised water: softening followed by reversed osmosis and electro deionisation. In the early years raw water was used. Feed water changed from softened to deionised in the 70s. Feed water is deaerated thermally. Water analysis covering: pH, conductivity, fluoride and calcium is performed every other week. The rate of water exchange per year is estimated to be 40%.

According to the Swedish Corrosion Institute, which has been responsible for all communication to and from the Värtan plant, the plant has no recent history of corrosion problems besides a case of cooling medium leaking from a heat exchanger.

The monitoring equipment is installed at the cold return at the heating plant.

Helsingin Energia (Finland)
The district heating distribution in Helsinki dates back to 1957. Since then the plant has been continuously extended and maintained. Thus several parts of the plant and network are newer. The network holds about 105,000 m^3 of water in 1,180 km of pipeline and delivers 3,075 MW to 12,400 consumers.

The forward temperature is about 85-115 °C and return about 40-80 °C (40-60 °C at the sampling point). The water is softened and thermally deaerated. A hydrazine hydrate oxygen

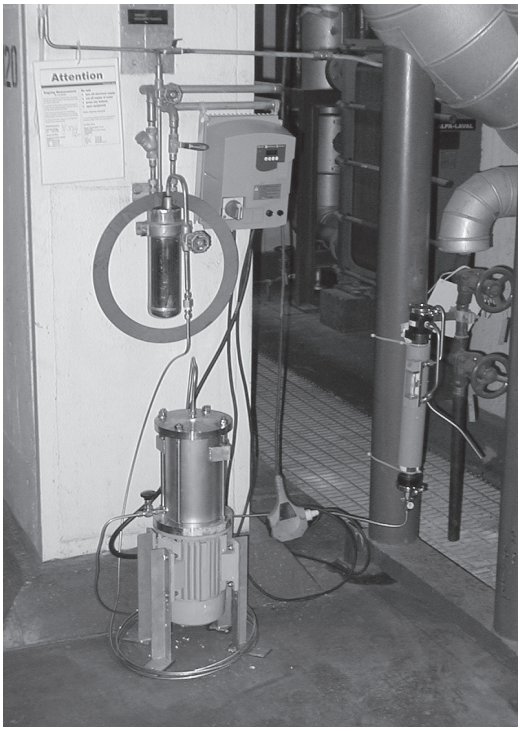


Figure 3.3 Installation of monitoring equipment in Helsinki.

scavenger is added as well as a pyranin staining chemical for leakage detection.

The following water quality parameters are measured every month: pH, conductivity, chloride, iron, copper, dissolved oxygen, and solids. Hardness, hydrazine hydrate and pyranin are measured five times per week.

According to our contact at the Helsingin Energia, they have not experienced any corrosion problems in the inside of the pipe. Some problems at the outside of the pipe have been encountered owing e.g. to leakage water.

The monitoring equipment is installed at the cold return at the heating plant

Aarhus Komunale Værker, Aarhus, Denmark
The plant delivers heat to the greater Aarhus area. Energy comes mainly from production of electricity at the Studstrup electrical power plant located north of the city. From the power plant heat is transported to the city in a transmission system. Heat is then transferred to a number of secondary networks through heat exchangers.

Two locations have been chosen at the Aarhus plant: one at the transmission line sampling water from the cold return pipe and one at one of the secondary networks delivering heat to the central part of town also sampling from the cold return.

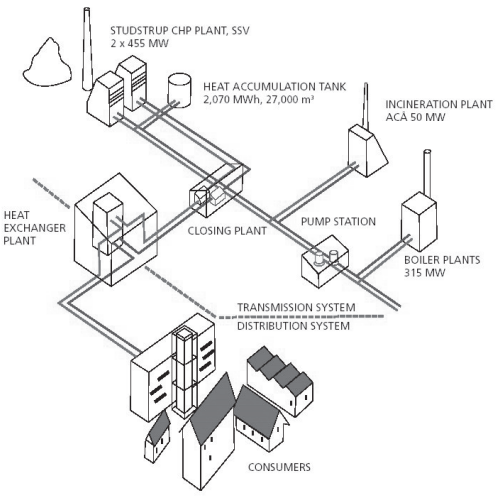


Figure 3.4 Illustration of the transmission and distribution networks in Aarhus.

Stadtwerke Lemgo GmbH – Lemgo, Germany
It has not been possible to obtain any data regarding the plant in Lemgo. Thus the age and size of the system as well as any history of corrosion problems are not known.

The monitoring equipment has been installed within the secondary distribution to a larger housing area. The sampling point was chosen to be on the cold return after a side stream filtration. The filter (10 µm) is not assumed to have any influence on the monitoring results.

Due to local regulations it was not possible to discard the water from the monitoring equipment to a drain. Thus, used water was pumped back into the system downstream of the sampling point.

The water in the network is treated with ”System Soft/SV” apparently a product that softens the water and increases the pH at the same time. Due to ”bacterial problems” addition of ”Hydro-X” is being tested at the moment.

Stadtwärme Lienz Produktions- und Vertriebs-GmbH – Lienz, Austria
The plant in Lienz was built 2001-2003 partly funded through the EU 5th framework programme. The project title was: ”Fuzzy logic controlled CHP plant for biomass fuels based on a highly efficient OCR-process”.

Energy for heat (60,000 MWh/year) and electricity (7,200 MWh/year) comes mainly from burning biomass. However, the plant is equipped with a 630 m^2 solar heat system that delivers 250 MWh/year.

Water is treated with trinatriumphosphate for pH adjustment and buffering. The following analyses are performed on a regular basis: pH, conductivity, p-value, m-value, hardness, iron and phosphate.

According to the plant personnel, no indications of corrosion problems have been encountered.

The monitoring equipment is located at the heating plant at the very point where the cold return enters the plant.

Southampton Geothermal – Southampton, United Kingdom

The system is 14 years old, and has at present approx. 15 km of underground pipe work distributed around the city. There are various heat inputs that serve the system: 2MW which works in conjunction with an absorption heat pump, 7MW of CHP (combined heating and power units), and 14 MW of conventional dual fuel boilers which run predominantly on gas.

The system operates with a supply temperature of between 80 and 85 °C and return temperature of between 50 and 55 °C. The sampling point chosen is located on the return line within the Heat Station at West Quay. The temperature at the sampling point is around 50 °C.

Water samples are taken once per week or more often as required. Analysis are carried out once per month by a water treatment company.

According to the plant personnel, the system has never suffered from any adverse corrosion problems.

The water is softened town water with sodium-meta-bisulphite added as an oxygen scavenger. The present chemical specifications are:

Pressure	4-5 bar
Hardness	12 ppm as $CaCO_3$
Alkalinity	370 (M) ppm as $CaCO_3$
TDS	555
Chloride	40
Sulphite	45 ppm
pH	8.8
Iron	< 0.5 ppm

3.2 Coupon exposure

Within the selected plants water was taken from the system and passed across a number of test surfaces before it was discarded to a drain (except in Lemgo).

Exposure chambers
Two different types of exposure units were utilised to simulate an exposure of metal to the plant water:

1) an exposure chamber simulating high velocity pipe flow, provided by the Danish Technological Institute.

2) an exposure chamber simulating stagnant water provided by the Swedish Corrosion Institute.

The unit simulating flowing water consist of an exposure cylinder where the test coupons (up to 30) are placed along the inner surface. A rotating cylinder placed in the center of the exposure cylinder creates a flow that may be varied by varying the rotation speed of the cylinder. Tilted axial holes through the rotating cylinder creates a cross flow that keeps the cylinder fully mixed.

The advantage of this unit is the ability to simulate pipe flow without having to spend more than about 1 litre of system water per hour. Another advantage is that the entire unit is constructed of AISI316 stainless steel, preventing the entrance of oxygen. The unit may be presurised to 40 bar, enabling in line monitoring without drainage of system water. The disadvantage is the cost of the unit. At the moment the sole cost of the chamber are about ecu 1,000.

The unit simulating stagnant water consist of a PVC pipe through which the water is passed slowly from bottom to top. Cylindrical coupons are ensembled using PVC spacers to a rod that goes inside the exposure chamber. The cylindrical coupons are thus exposed on the outside.

The flow across the surface of the coupons depends on the flow through the exposure chamber, which is one of the disadvantages of this type of exposure chamber. The chamber can not be pressurised and the effluent must therefore either be led to a drain or pumped into the system again using a pump. The transparent PVC pipe used is not impermeable to oxygen and it may thus be assumed that the oxygen concentration within the chamber will increase as the flow through the chamber is lowered. One advantage of the chamber is though the cost which is expected to be significantly lower than the above unit.

Installation
Monitoring equipment consisting of both types of exposure chambers were installed at all ten involved plants. Water from the sampling point was first led through the flowing water unit then through the stagnant water unit and finally led to the drain (except in Lemgo).

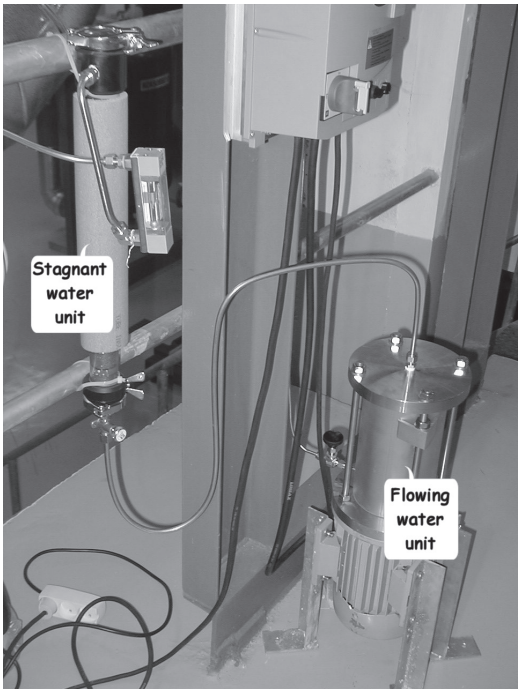


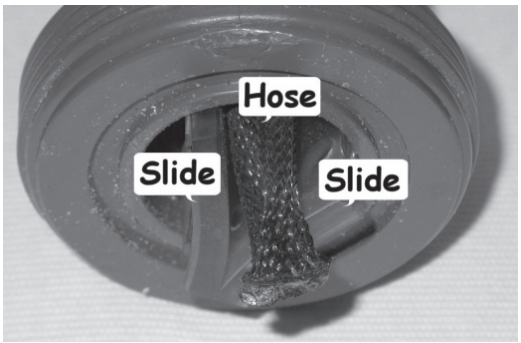
Figure 3.5 Typical installation showing the two types of exposure chambers.

The stagnant water units were delivered fully equipped with coupons from the Swedish Corrosion Institute, whereas the coupons for the flowing water unit were kept in a dry and anaerobic environment until the equipment was installed.

Equipment and coupons were installed by the Danish Technological Institute during the fall of 2003. The dates of installation are listed below.

Budapest	September 25, 2003
Děčín	October 24, 2003
Stockholm (Hässelby)	September 18, 2003
Stockholm (Värtan)	November 4, 2003
Helsinki	October 23, 2003
Aarhus (transmission)	August 15, 2003
Aarhus (distribution)	August 15, 2003
Lemgo	October 2, 2003
Lienz	October 3, 2003
Southampton	October 9, 2003

Figure 3.6 image showing two slides from the flowing water unit (each with three coupons mounted) placed inside a transport cylinder. The perforated hose contains silica gel for moisture adsorbtion.



Exposed samples were collected by the plant personnel according to oral (given during installation) and written instructions from the Danish Technological Institute. Samples were collected after roughly 3, 6, and 9 months of exposure.

Coupons from the flowing water unit were retracted on the polycarbonate slides on which they were mounted. At each sampling two slides with each three coupons (three different metals) were retracted, dried using nitrogen gas and sealed in a shipping container with a 2 bar nitrogen atmosphere. At retrieval at the Danish Technological Institute the pressure of the shipping containers was tested prior to opening.

Coupons from the stagnant water unit were disconnected from the sample rod and transferred to test tubes filled with system water. To lower the oxygen penetration through the polycarbonate test tube, the procedure was improved by placing the tube inside a larger flask filled with nitrogen gas.

Figure 3.7 Sampling and shipping of coupons from the stagnant water unit. The inner tube is filled with system water, while the outer flask is filled with nitrogen gas.

3.3 Analytical methods - pipe flow simulation

Corrosion monitoring units (CMUs) that were based on the rotortorque principle [Griebe and Flemming 2000] were installed on a side stream of the return circuit of each DH systems in order to expose the test coupons to in situ conditions.

Test coupons were flat, with a surface area of 14.4cm^2 (2.4 cm wide by 6.0 cm long)

Test coupons of mild steel (SAE 1015) were coated on the back side with chemically and electrochemically inert diamond-like-carbon (Ibad DLC). The coupons were cleaned according to ASTM standard (G1-03) [ASTM, 2003] and weighed prior to exposure.

Coupons were fixed on polycarbonate slides.

The flow through the CMUs was approx. 1 l/h (hydraulic resistance time of approx. 1 hour) with turbulent conditions (surface velocity at approx. 2 m/s) imitating the conditions of an average DH pipe. The CMUs were run at room temperature at their respective location yielding an internal temperature within the range of 30-40°C.

At retrieval, coupons used for corrosion measurements were dried on site by the use of oxygen-free N_2.

In order to evaluate corrosion, deposits and microbiological aspects, the following analysis were performed for all sample sets retracted from the unit simulating flowing water:

- Visual inspection
- Measurements of general corrosion rate
- Measurements of localised corrosion rate
- Presence of sulphides within deposit
- Total number of bacteria
- Sulphate reducing bacteria

Treatment at arrival
Retracted coupons were photographed on arrival to the Danish Technological Institute in order to document the appearance of surface deposits and corrosion products.

Half of the coupons were used for microbiological analyses as described below.

Visual inspection
The other half of the coupons were investigated under a stereo microscope (up to 63x magnification) to identify possible localised attacks.

Evaluation of corrosion
Corrosion of mild steel coupons was addressed by measurements of weight loss and pit formation. Corrosion of stainless steel and copper was solely addressed by measurements of pitting and crevice (stainless steel) corrosion.

General corrosion rate
Corrosion rates of mild steel were measured by weight loss according to ASTM G1-03. Briefly, prepared coupons (see elsewhere) were cleaned and weighed prior to exposure. Retracted coupons were cleaned by sonication for 5-20 minutes in concentrated hydrochloric acid inhibited with 20g Sb_2O_3, 50g $SnCl_2$, and 6g CuCl (Corrosion **59** 11, 1029 2003) per 1000ml. After rinsing in de-ionised water, drying, sonication in acetone (to remove traces of water), and drying in nitrogen gas, coupons were kept in a desiccator over silica gel until weighing.

Corrosion rates of coupons treated and exposed in similar maners in three Danish district heating systems [Smidt and Frølund 1998] have previously been evaluated statistically according to ASTM G16-95. The results showed that corrosion rates were independent of position within the annular exposure chamber.

Localised corrosion
Pit formation was identified by visual inspection. For mild steel coupons, up to seven individual pits were selected [ASTM G46-94] for detailed depth profiling by laser interferometry [UBM 2003].

UBM Microfocus COMPACT is an opto-electronic 3D measurement system for non-contact measurement and analysis of surfaces. The method of the Microfocus sensor is based on the principle of “Dynamic focusing”. A laser beam with a spot size of 1µm is used to scan the surface. This technique allows soft and touch-sensitive surfaces to be quantified. The system is provided with sub-micron resolution in all axes, thus enabling accurate determination of 3D surface features without limitation of point density.

A pitting corrosion rate was calculated based on average and standard deviation of measured pit depths. According to ASTM G46-94, a pitting factor was calculated for mild steel coupons based on the maximum pit depth and the general corrosion rate based on weight loss.

Localised corrosion of copper and stainless steel was evaluated in similar manners. Stainless steel coupons (consisting of two thin plates welded together) were dismantled prior to inspection in order to address crevice corrosion between the plates.

Retracted coupons were cleaned according to ASTM G1-03. Briefly the following procedures were followed:

Copper coupons were sonicated for 1-3 minutes in concentrated hydrochloric acid mixed 1:1 with de-ionised water. Rinsed and dried as described for mild steel. Stainless steel coupons were sonicated for 20 min in a 1:10 mixture of nitric acid and de-ionised water at 60°C. Rinsed and dried as described for mild steel.

For copper and stainless steel, localised corrosion rates were calculated based on maximum pit depth.

Deposit chemistry

Presence of sulphides
Sulphide in the biofilm was determined semi quantitatively with a method based on catalytic formation of nitrogen bubbles observed in a light microscope (Zeiss) due to an azide-sulfide reaction [Feigl et. al., 1972].

Microbiology on surfaces
Biofilm was scraped off the coupon surfaces by use of sterile cell scrapers (Orange Scientific), stored in filter-sterilised deionised water (Millipore, 0.2µm). Before analysis the biofilm was homogenised manually with a 0.5 mm glass homogeniser (Thomas Scientific, USA). Sub samples for counting total number of bacteria were preserved with formaldehyde (2% final concentration, v/v). Unpreserved sub samples were used for determination of sulphate reducing bacteria.

Total number of bacteria
Determination of total number of bacteria was performed in biofilm samples by the general bacterial stain DAPI (4´,6-diamidino-2-phenylindole) and use of fluorescence microscopy [American Public Health Association/American Water Works Association/Water Environment Federation, 1995]. A Zeiss Epi-fluorescence microscope with the filter set 01 and 100x magnification objective for oil was used. The counting was performed on black polycarbonate filters (Osmonics Inc.), where 10 randomly chosen fields (100x100 µm) were selected. Within each of those fields 20-200 cells were counted, with a minimum of 400 cells in total per filter.

Problems with enumeration in samples containing abundant corrosion products were solved by use of either a citric acid/citrate or glycine/sodium hydroxide buffer with pH 3 to remove the interference with counting.

Sulphate reducing bacteria (cultivation)
The presence of SRBs was evaluated by cultivation using a modified Postgate C medium [Postgate, 1984]. SRBs were determined to be present when production of sulphide could be measured. Sulphide was measured colorimetrically by the methylene blue method according to [Cline 1969]. The media was inoculated under mesophilic (35°C) conditions.

3.4 Analytical methods - stagnant water simulation

Equipment
The main part of this exposure container consists of a cylinder of PVC plastic, with the length of 500 mm, and with a diameter of 50 mm (see figure 3.8). On the surface of the cylinder a probe of a thermometer is connected, and just before the inflow to the exposure container a needle valve and a flow meter are connected.

In the cylinder there is a chain of connected but separable pieces, also made of PVC plastic, on which cylindrical formed coupons are located (see figure 3.8). For every coupon a rubber ring is located at each end of the coupon, avoiding water to penetrate to the inner surface of the coupon. On the top of the exposure container, there is a tight-fitting lid that can be removed, and the inner plastic chain with the coupons lifted. When sampling, the inner plastic chain is lifted so that only the coupons that shall be withdrawn are exposed to air. Then these coupons are withdrawn, the empty plastic piece is put back, and the inner plastic chain is lowered into the exposure container (and the exposure process continues for the rest of the coupons).

Samples and sample handling
Like the equipment for pipe flow simulation the corrosion monitoring unit for stagnant conditions was installed in a side stream of the return line of each DH system in order to expose the test coupons in situ.

Water flow through these units was set to 1-2 l/h giving an average flow velocity of 1-2 cm/min and a hydraulic retention time of about one hour.

The coupon material was seamless carbon steel. The coupons were formed as cylinders with the dimensions height 2.5 cm, inner diameter 1.9cm and outer diameter 2.2 cm. Before exposure the coupons were pickled, rinsed in ethanol, air-dried and weighed.

At every sampling occasion three coupons were withdrawn, and the coupons were placed in separate bottles. Also water samples were taken at some occasions. Before filling the bottles, the system water was allowed to pour a short while. After sampling, the samples were sent directly to Stockholm for analyses. Depending of delivering time this could result in a waiting time of at a maximum five days. To loosen the biofilm the bottles with the coupons were placed in an ultrasound bath for 1 minute and thereafter shaken for an additional 5 minutes. The coupons were picked up from the bottle with sterilised tweezers, rinsed in ethanol, dried by a burner flame and weighed. Finally the coupons were investigated optically. The bottles with the water sample and the bottles with the loosened biofilm were investigated using microbiological technique.

Microbiological analyses

General
Determination of present microorganisms in water and biofilm samples from these units has

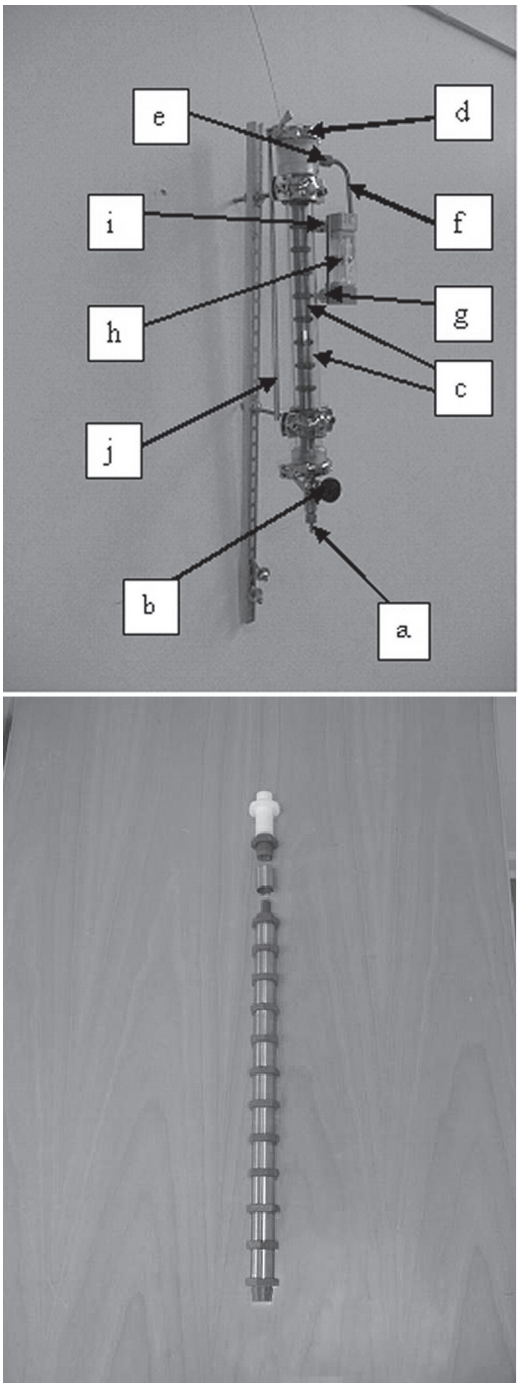


Figure 3.8. Exposure container. Top, exposure container with belonging units: a) inlet from district net, b) regulator for flow, c) coupons (sitting on separable plastic units), d) opening for successive withdrawal of coupons, e) outlet from exposure container to flow meter, f) connection between exposure container and flow meter, g) flow meter, h) inlet to flow meter from exposure container, i) outlet from flow meter to waste (connection to "waste tube" behind the exposure container), j) tube for connection to waste. Bottom, the inner part of the exposure container: sequence of coupons on separable plastic units, where the top plastic unit and the belonging coupon have been detached. The white piece is a holder from which the inner part hangs in the exposure container.

been of two kinds; the presence of three types of organisms in viable forms and the total presence of organisms (i.e. all kinds of microorganisms, and both dead and viable). The groups of viable microorganisms which were determined were the group of aerobic heterotrophic bacteria, the group of sulphate reducing bacteria (SRB), and the group of fungi. The district heating water and the solutions with loosened biofilm were exposed to specific nutrient media for each group of microorganisms. The nutrient media for aerobic heterotrophic bacteria were nutrient agar (NA, Merck no. 1.05450) and plate count agar (PCA, Merck no. 1.05463), while for fungi malt extract agar (MA, Merck no. 1.05398) was used. For these two groups plate counts on agar gel were performed while for SRB Postgate medium B was used. All the liquid preparations and the following handling were made following normal, sterile, microbiological routines. For determination of the total amount of both viable and dead microorganisms no special solutions were used.

Plate counts

To estimate the concentration of viable agar gel growing microorganisms, 0.1ml of each sample solution was spread on triplicates of agar gel plates containing MA, NA and PCA agar, respectively. The agar plates were incubated aerobically at 22 ºC ± 2 ºC (room temperature) at 50% relative humidity and colonies were counted after 3, 7 and 14 days.

Sulphate reducing bacteria

To estimate the concentration of viable sulphate reducing bacteria, SRB, in the biofilms on the coupons or in the district water of the nets, anaerobic glass vials with Postgate medium B and sealed with a oxygen impermeable Tyrene ™ stopper were after inoculation with 1 ml sample placed in an incubator at 37 ºC ± 1 ºC. Three serial tenfold dilutions of the original samples were performed in triplicate. Blackening of the medium due to FeS formation indicated sulphate reduction and, thus, SRB activity. A maximum of 28 days was permitted for the vials to change colour for the evaluation of the results. The number of SRB were estimated using the MPN method (Microbiologically Influenced Corrosion. B J Little, F Mansfeld & P A Wagner. NACE International 1997).

Total Cell Count

The total amount of microorganisms was estimated by using an improved Neubauer counting chamber and a light microscope with a 40x magnification lens (plus 10x in the ocular). This chamber has an intervening space of 0.1 mm, and one of the plates is equipped with a grid where the squares had a size of 0.0025 mm^2. A droplet of the sample solution was applied at the edge of the chamber, resulting in filling of the intervening space due to the capillary force. The filled chamber was then placed under a microscope at 400 times magnification, followed by counting of the microorganisms in ten squares. The concentration of the sample solution was calculated by utilising the known volume of the counted squares (0.00025 mm^3).

4 Results of survey

The results of the analysis performed on the exposed coupons are divided into two sections, one for each exposure unit. The results and the methods used are hereafter discussed.

A basic array of analysis have been performed on all three sets of samples retracted, except for the third set of samples from the stagnant water unit.

Due to lack of manpower at the Swedish Corrosion Institute, it was decided that the project would benefit the most from testing of advanced electrochemical methods for analysing MIC compared to performing the third and last set of analysis on these coupons.

The results from the basic analysis scheme are given below.

4.1 Corrosion and fouling - pipe flow simulation

Samples were taken out by the plant personnel on three occasions: after roughly 3, 6, and 9 months of exposure. The plant personnel were instructed during the installation of the equipment. They were thus able to handle the samples in a way that microbiological contamination of the samples was prevented and oxidation of the sample by atmospheric air was kept at a minimum.

All samples were sealed inside transparent cylinders and flushed and pressurised with nitrogen gas prior to shipping. At arrival at the Danish Technological Institute the pressure of nitrogen was assured and maintained until analysis.

At the day of arrival pictures of the samples were taken in order to track any changes in oxidation state due to inadequate storage. No such oxidation took place.

Figure 4.1 and figure 4.2 shows the samples from the first and the third sampling as they looked upon arrival at the Danish Technological Institute.

Figure 4.1 pictures taken of the coupons from the first sampling from the flowing water unit

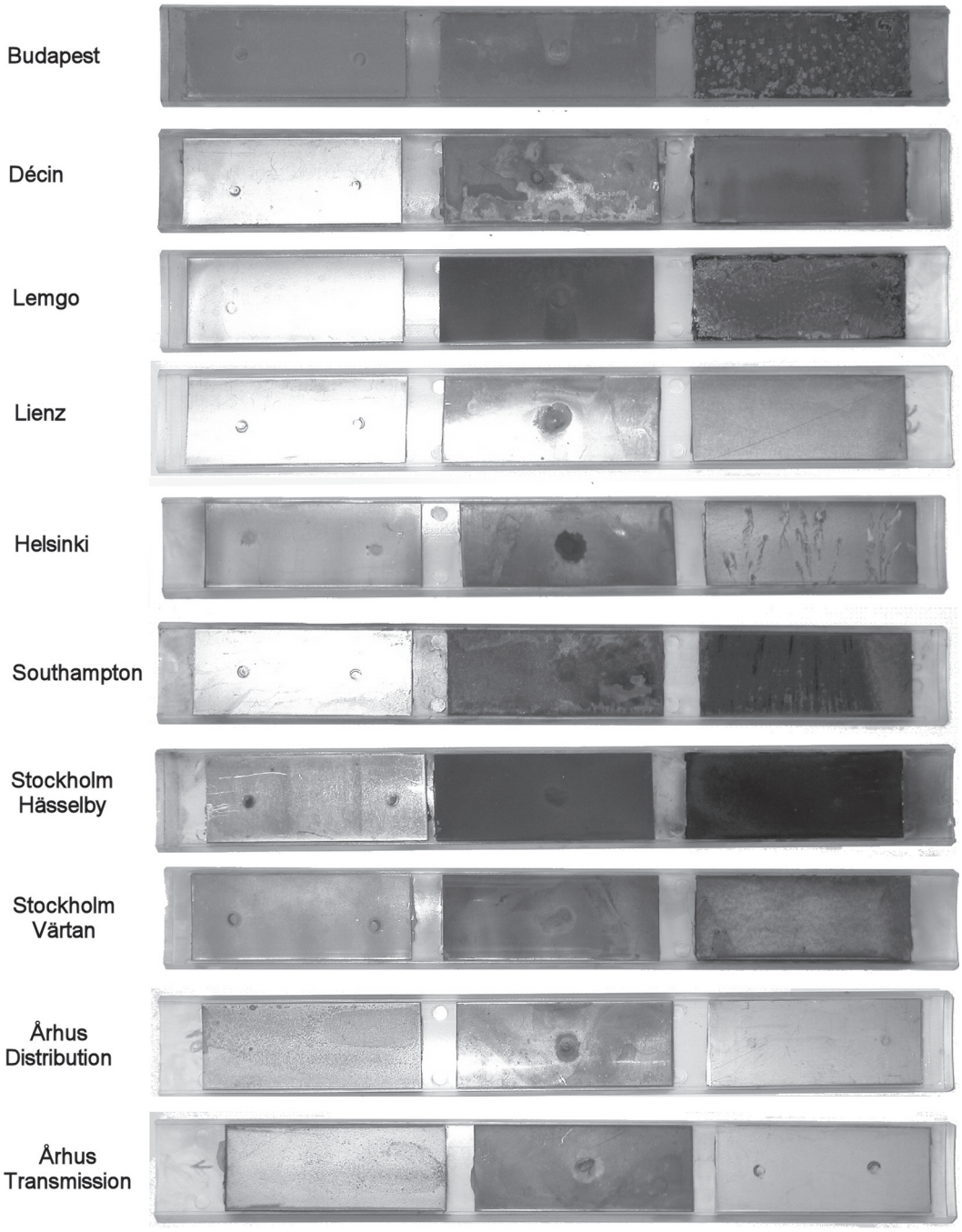


Figure 4.2 pictures taken of the coupons from the third sampling from the flowing water unit

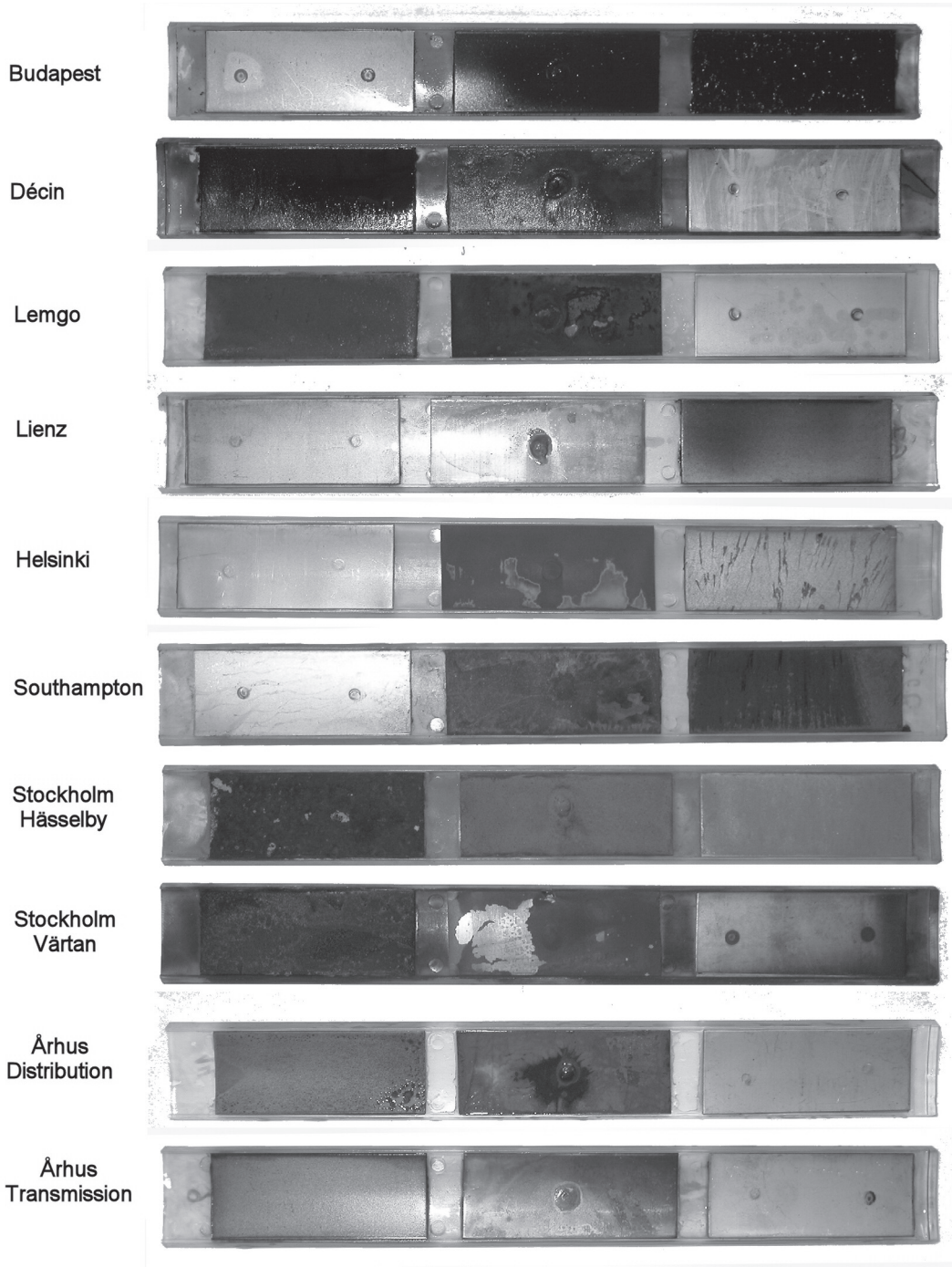


Figure 4.3 biofouling of mild steel coupons as total number of cells per cm²

Figure 4.4 biofouling of copper coupons as total number of cells per cm²

Figure 4.5 biofouling of stainless steel coupons as total number of cells per cm²

Biofouling

The amount of biofilm on the three coupon materials were addressed by scraping off the biofilm and counting the total number of cells.

The results are shown in figure 4.3-4.5.

Total number of bacterial cells on the surfaces of the coupons ranged from 10^3 to more than 10^7 cells/cm². The lowest overall degrees of fouling were found at the two Aarhus sites, Lienz and Helsinki.

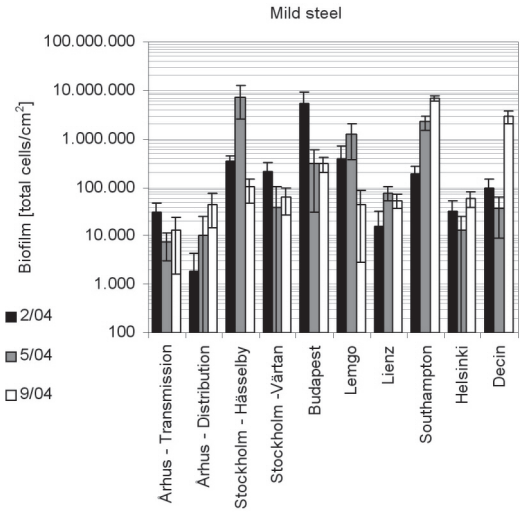
Looking at the development of biofouling at the sites both stagnant and exponentially increasing changes may be observed. The exponential increase is clearly depicted for e.g. copper at Southampton and Děčín, whereas the stagnant conditions may be observed for mild steel at e.g. Aarhus, transmission or Helsinki.

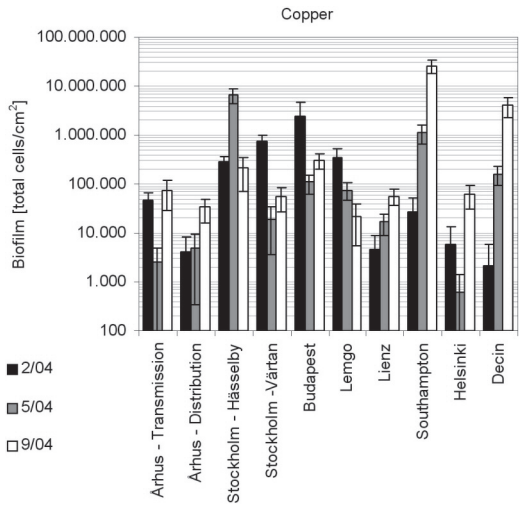
It seems that the amount of biofilm on stainless steel approaches the same level of 10^4-10^5 cells/cm² for all sites. This may be due to the fact that the surface of the stainless steel is rather smooth compared to e.g. the mild steel which at some sites is covered with corrosion products. The limit for biofouling on stainless steel may be caused by the biofilm sloughing off at a certain thickness.

Based on our previous observations throughout the Danish DH industry, we would expect the possibility of MIC to be significantly at: Hässelby (Stockholm), Budapest, Lemgo, Southampton, and to some extent Děčín. The total cell number found at the two Aarhus sites, Lienz, Helsinki and to some extent Värtan (Stockholm) does not indicate an elevated risk of MIC compared to previous experiences in Denmark. However only a thin biofilm at the wrong place is necessary to initiate MIC, particularly in DH systems where the ionic strength and buffer capacity are low.

Sulphate reduction

Only in two cases a low production of sulphide could be identified: On biofilm from stainless steel exposed in Děčín and in Stockholm - Hässelby. The remaining samples did not show any sulphide production within the 30 day incubation.





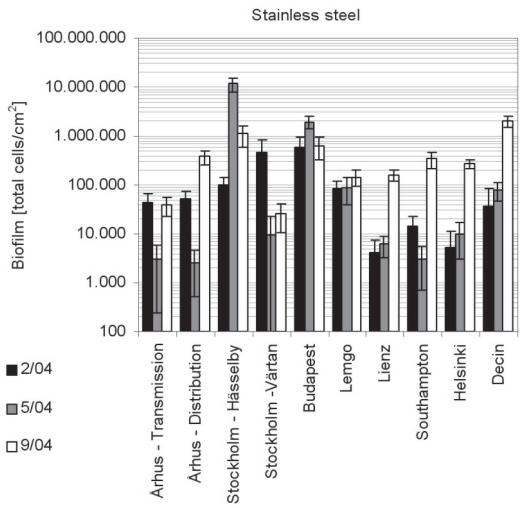


Figure 4.6 General corrosion rates for mild steel coupons exposed in the flowing water unit.

Figure 4.7 local corrosion rates for mild steel coupons exposed in the flowing water unit.

Figure 4.8 Pitting factors calculated for mild steel coupons exposed in the flowing water unit.

Corrosion

Corrosion of the mild steel coupons were addressed both by a general corrosion rate through weight loss and a local corrosion rate through measurements of pit depths.

The general corrosion rate was measured shortly after the coupons were received at the Danish Technological Institute in order to minimise the risk of corrosion after sampling.

The measured general corrosion rates ranged from a few micrometer per year to about 40µm/year. The general corrosion rates are shown in figure 4.6.

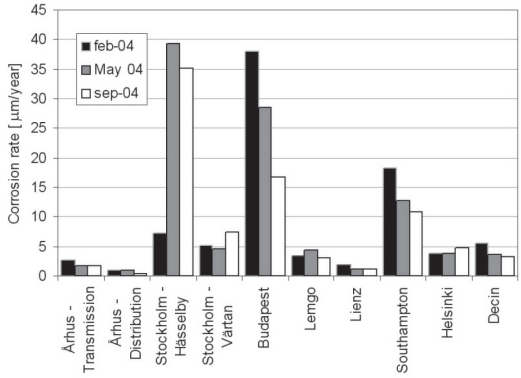
The lowest rates were seen at the two Aarhus sites and at Lienz, where the maximum corrosion rate throughout the entire monitoring period did not exceed 2.5µm/year. The rate for Värtan (Stockholm), Lemgo, Helsinki, and Děčín was slightly higher, around 4-6µm/year. The remaining three sites: Hässelby (Stockholm), Budapest and Southampton, showed rates between 10 and 40µm/year.

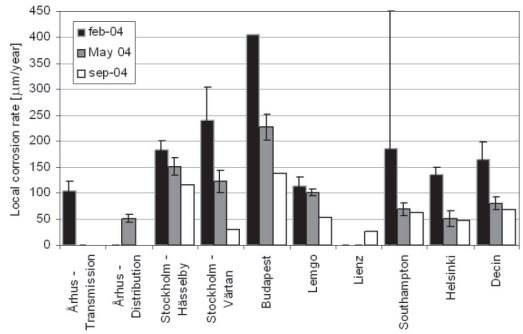
The general corrosion rate for some of the sites, e.g. Budapest and Southampton, decreased from the first over the second to the third sampling, owing probably to the fact that corrosion products build up at the surface limited the corrosion of the underlying metal.

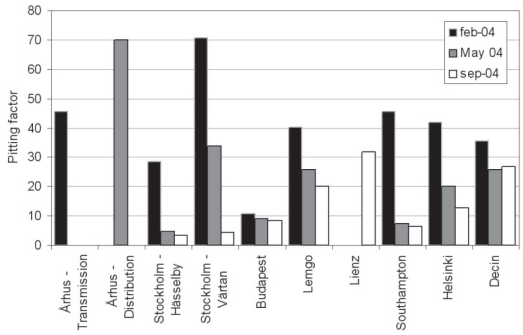
All measured rated are relatively low compared to the expected lifetime of the DH installations and the wall thickness of the installations. Even at the highest measured rate of 40µm/year it would take 25 years to corrode one millimetre of the wall thickness. However, looking at the local corrosion rate, the situation changes.

Local corrosion rates ranged from a few cases of no localised corrosion at all to pits formed at a rate of 400µm/year. An example of a pit measurement is given in figure 4.9.

The lowest rates were found at the two Aarhus sites, Lemgo and Lienz, where the maximum local corrosion rate did not exceed 100µm/year. The local corrosion rate was generally highest at the first sampling after three months of exposure and dropped at the second and third sampling. It may thus be assumed that the processes creating the local corrosion attacks are most dominant on fresh coupons and levels off as the coupons are covered with corrosion products.







At the two Stockholm sites, Budapest, and Lemgo, the local corrosion rate stayed at an elevated level for at least two sample periods. This indicated that the processes were not significantly limited by the buildup of corrosion products on the coupon surface, as it would probably be the case if the corrosion was solely of a chemical nature.

A pitting factor was calculated as the ratio of the maximum local corrosion rate (based on the maximum pit depth) to the general corrosion rate. Figure 4.8 shows calculated pitting factors. It may be observed that the pitting factor ranges from practically zero to about 80.

The highest pitting factors are found at the Aarhus sites where the general corrosion rate is very low. This means that almost all of the corrosion that takes place on these coupons is localised. On the other hand, some of the sites

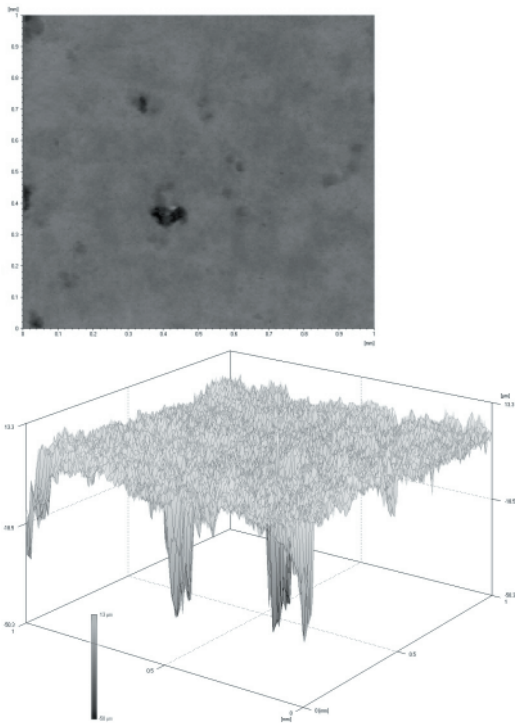


Figure 4.9 Topographical representation of pits on a mild steel coupon from the Southampton plant. Scan size: 1x1 mm. Z-scale ranging from -50 to 13 micrometers.

with a high general corrosion rate show a low pitting factor (e.g. Budapest) indicating that even though the local corrosion rate is high a large part of the general corrosion is caused by uniform corrosion.

Presence of sulphides

Sulphides in the form of solid minerals like iron sulphate and copper sulphide was identified on the coupon surfaces using a semi quantitative spot test. The response to the test was given a score between zero and three, zero being no reaction and three being a very rapid reaction as indication of a high concentration of sulphides. The test was performed on all material types and averaged over the entire test period for each material (see figure 4.10)

Sulphide on copper surfaces was only in a few cases (Budapest and the two Stockholm sites) present in significant amounts. For the two other material types sulphide was present in significant levels on all coupons. On mild steel, which were used for the corrosion measurements, no particular difference within the sulphide presence could be detected. However, using the overall image of sulphide on all three materials the sites differ quite a lot. Lemgo and Aarhus - Transmission resides in the lower end of the spectrum while Budapest, Lienz, Southampton and the two Stockholm sites top.

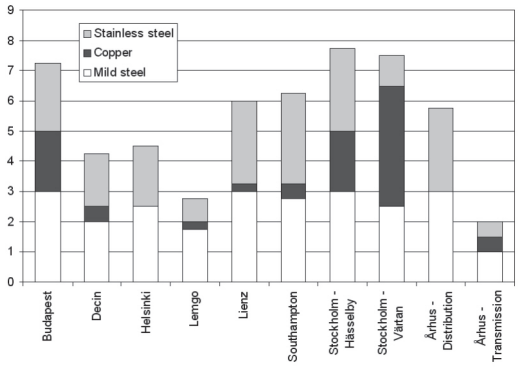
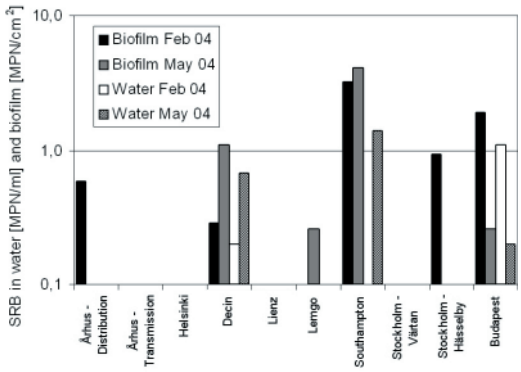


Figure 4.10 Semi quantitative measure of sulphides on coupons given as averages over the entire test period.

4.2 Corrosion and fouling - stagnant water

Figure 4.11 Cell numbers in water and biofilm from the stagnant water unit



Microbial analyses

Fungi
Aerobic fungi were detected at 5 different locations and with one exception (a water sample from Budapest) only in biofilm samples. Only in Lienz could a low level of fungi be detected on both sampling occasions, while the other sites just showed presence of fungi in one sample. The amount of aerobic fungi in biofilm was relatively high in Budapest and Stockholm (V) being $1{,}2 \cdot 10^5$ and $1{,}6 \cdot 10^5$ cells/cm^2 respectively.

Bacteria in water samples
The amounts of culturable, aerobic, heterotrophic bacteria in the water phase were generally low, being between 0 and $4{,}0 \cdot 10^4$ cells/ml, independent of the used type of agar. No culturable bacteria were found in Helsinki, Lemgo and Southampton.

At the same time the found total counts of microorganisms by direct light microscopy in general show levels of approximately $1 \cdot 10^6$ cells/ml for the majority of samples. In 5 of 20 water samples no microorganisms were observed under the microscope. With the exception of Helsinki where neither approach (growth on agar or microscopy) could detect any bacteria these findings were independent of the amount of heterotrophic growth observed on the agar plates.

Table 4.1. Concentration of viable microorganisms in water samples. Estimated by using malt extract agar (MA), nutrient agar (NA), plate count agar (PCA) and concentration of total bacteria (both viable and dead) determined by light microscopy (total counts).

DH System	Aerobic incubations on agar			Total counts
	MA	NA	PCA	
Aarhus (D)	0	4.0E+04	4.0E+04	8.0E+05 2.0E+06
Aarhus (T)	0	4.0E+03	8.0E+03	0 4.0E+05
Helsinki	0	0	0	0 2.0E+06
Děčín	0	6.1E+02	4.6E+02	3.6E+06 5.6E+06
Lienz	0	2.4E+04	3.2E+04	0 1.6E+06
Lemgo	0	0	0	2.8E+06 1.2E+06
Southampton	0	0	0	4.0E+06 0
Stockholm (V)	0	4.0E+04	4.0E+04	1.2E+06 3.2E+06
Stockholm (H)	0	8.0E+03	1.2E+04	0 2.0E+06
Budapest	3.2E+04	3.2E+04	3.2E+04	2.8E+06 1.2E+06

Bacteria in biofilm
The occurrence of culturable, aerobic, heterotrophic bacteria in biofilm varied from 0 (in 9 of 40 incubations) up to $8{,}3 \cdot 10^5$ cells/cm^2. The PCA agar gave in general figures that were somewhat (up to 90%) lower than parallel incubations with NA agar. Total counts of biofilm microorganisms all showed numbers ranging from $3{,}8 \cdot 10^7$ to $3{,}3 \cdot 10^8$ cells/cm^2, irrespectively of the level of occurrence of heterotrophic growth.

Table 4.2. Concentration of viable microorganisms in biofilm. Estimated by using malt extract agar (MA), nutrient agar (NA), plate count agar (PCA) and concentration of total bacteria (both viable and dead) determined by light microscopy (total counts).

DH System	Aerobic incubations on agar			Total counts
	MA	NA	PCA	
Aarhus (D)	0 0	8.3E+05 1.3E+05	4.0E+04 9.9E+04	8.3E+07 2.3E+08
Aarhus (T)	0 0	4.5E+05 0	8.0E+03 0	1.1E+08 3.3E+08
Helsinki	0 0	1.3E+05 3.0E+04	0 8.9E+04	1.2E+08 9.6E+07
Děčín	0 4.9E+02	1.0E+05 1.0E+05	4.6E+02 5.3E+04	1.8E+08 1.2E+08
Lienz	7.0E+02 2.1E+02	3.0E+04 3.7E+04	3.2E+04 2.1E+04	9.9E+07 1.1E+07
Lemgo	0 0	1.3E+05 0	0 0	1.6E+08 1.4E+08
Southampton	6.5E+01 0	1.6E+05 4.7E+04	0 3.1E+04	1.7E+08 7.8E+07
Stockholm (V)	1.6E+05 0	4.6E+05 1.2E+04	4.0E+04 1.0E+04	4.1E+07 5.5E+07
Stockholm (H)	0 0	1.9E+04 0	1.2E+04 0	6.0E+07 1.5E+08
Budapest	1.2E+05 0	1.2E+05 2.8E+04	3.2E+04 6.7E+03	3.8E+07 1.2E+08

Figure 4.12. Corrosion rates from the stagnant water unit

Corrosion

General corrosion was measured by weight loss on all the retrieved coupons. The found corrosion rates were between 0.6 µm/year (Southampton) and 36 µm/year (Stockholm (H)), with the last value differing somewhat from the rest. In general the corrosion rate had decreased at the second sampling compared to the first sampling. The only exception was Stockholm (H), where the rate did increase from 19 to 36 µm/year.

This site was also the only plant where pits could be seen. The pits were in the form of shallow depressions (see figure 4.13) with a diameter of up to 5 mm. Due to the curvature of the coupon it was not possible to measure the depth of the pits.

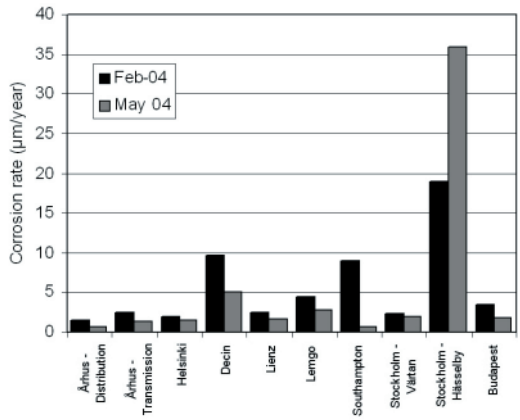
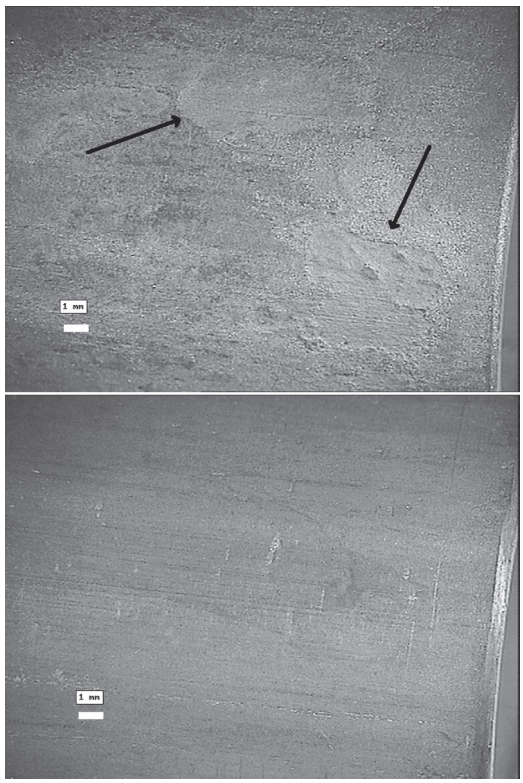


Figure 4.13. Surface of exposed (Top) and unexposed (Bottom) coupons from the Hässelby plant of Stockholm. At the exposed surface shallow depression can be seen. The white rectangle has a length of 1 mm.



4.3 Evaluation of MIC

Results from the basic analysis performed on exposed coupons within the ten plants show large variations in corrosion attacks and degree of fouling. In the following the results are evaluated in terms of characterising the corrosion within each plant as either MIC or non-MIC.

Biofilm
The amount of biofilm bacteria on the mild steel coupons may in terms indicate the probability of MIC. A large number of cells is, other things being equal, assumed to create a higher probability of MIC than a low number.

Looking at the results for total bacterial counts in biofilm using the DAPI staining method, the cell numbers vary from 10^3 to 10^7 cells/cm^2. Four plants stand out in that the biofilm cell concentration does not exceed 10^5 cells/cm^2 at any point during the survey: The two Aarhus sites, Lienz, and Helsinki. The plant in Děčín starts out at the same level at the first two samplings but takes off and reaches $3 \cdot 10^6$ cells/cm^2 at the third sampling.

Three plants started out quite high at 10^5-10^7 and dropped to 10^5 or lower at the last sampling: The two Stockholm plants and Lemgo. The plant in Budapest also started out with a relatively high concentration but did only drop to about $3 \cdot 10^5$ cells/cm^2.

The Southampton plant and the Aarhus - Distribution plant were the only ones where the biofilm concentration kept rising during the survey. In Southampton the concentration went up from $2 \cdot 10^5$ to $7 \cdot 10^6$ cells/cm^2, while the concentration in the Aarhus - Distribution plant went from $2 \cdot 10^3$ to $4 \cdot 10^4$ cells/cm^2.

Based on these developments and the above assumption, the highest possibility of MIC should be found in: Stockholm - Hässelby, Budapest, Lemgo, and Southampton. The sudden change in Děčín at the third sampling may also indicate a relatively high possibility for MIC.

On the other hand determination of biofilm bacteria by light microscopy of samples retrieved from stagnant conditions showed very similar bacterial numbers in all samples ranging from $1.1 \cdot 10^7$ to $3.3 \cdot 10^8$ cells/cm^2. These data seem to be in conflict with the above mentioned data obtained by fluorescence microscopy. They also imply a medium to high risk for MIC based on former experience by the Swedish Corrosion Institute.

Additionally, it is worth noting that there have been detected viable, heterotrophic, aerobic bacteria in biofilm from all plants with values up to $4.6 \cdot 10^5$ cfu/cm^2. Occurrence of bacteria capable of growing on nutrient-rich agar under aerobic conditions can indicate recent intrusion of oxygen or raw water into the DH systems. Solid interpretation of these data would require detailed information on possible intrusions of oxygen or raw water at any particular plant. Unfortunately, this information was not available.

Sulphate reducing bacteria
The sulphate reducing bacteria have been acknowledged in Denmark as one of the main contributors to MIC in DH systems. In Denmark, the SRB are usually identified through their ability to reduce sulphate to sulphide in an artificial medium adjusted to reflect the ionic strength in DH water.

Results from this survey on sulphate reduction does, however, only turn out slightly positive for two biofilm samples taken from stainless steel coupons.

Growth based MPN analysis on coupons from the stagnant water unit shows positive results in six out of ten sites at the first sampling and four out of ten at the second. The numbers, though, do not exceed 5 culturable SRB cells/cm^2.

Four plants did not show any positive SRB results at all: Aarhus - Transmission, Helsinki, Lienz, and Stockholm - Värtan. Thus, these four plants are assumed to experience a lower probability for MIC than the other six.

Sulphide minerals
Presence of sulphide minerals, detected on coupons from the flowing water unit using a spot test, turned out positive at all ten sites. The overall concentration on all three coupon metals was lowest at Lemgo and Aarhus - Transmission, while the highest concentrations were found at Budapest and the two Stockholm sites.

The sulphide detected can only originate from two sources: it is either added to the system through the feed water, which is highly unlikely, or it is produced in the system through biological sulphate reduction. The presence of sulphide is therefore an indirect indication of the presence of sulphide reducing bacteria regardless that the growth based methods did not show any.

The question now remains: why do some of the sites corrode so heavily and some not, when all of them have SRB present?

Corrosion
Corrosion has been evaluated through a general corrosion rate as determined through weight loss and a localised corrosion rate determined through direct measurements of pit depth. A pitting factor calculated as the ratio between the general corrosion rate and the corrosion rate for the deepest pit has also been used to evaluate corrosion.

General corrosion
The general corrosion rate obtained from the two different exposure units does not correlate. The following evaluation is thus based entirely on the corrosion data from the flowing water unit.

General corrosion rates range from a few µm/year to about 40µm/year. The lowest rates are found at the two Aarhus sites, Stockholm - Värtan, Lemgo, Lienz, Helsinki, and Děčín, which experienced a maximum of 8µm/year during the entire survey. The three remaining sites: Stockholm - Hässelby, Budapest, and Southampton experienced a significantly higher general corrosion rate. Stockholm - Hässelby started out rather low but escalated to 35-40µm/year. Budapest on the other hand started high at about 35µm/year and dropped to 15µm/year at the third sampling. Southampton, having the third highest general corrosion rate, started at 18µm/year and dropped to 10µm/year at the third sampling.

Looking at the general corrosion rate as a measure of residual life time for the plants, the only plants that experience significant lifetime reduction is Stockholm - Hässelby and Budapest with a maximum rate of 1mm per 25 years.

Localised corrosion
Looking at the localised corrosion rate instead, the image is somewhat changed. The rates ranged from no localised corrosion to rates of 400µm/year. The two Aarhus sites, Lemgo and Lienz did dot exceed 100µm/year, while Budapest topped with 400µm/year at the first sampling. The remaining sites varied between 150 and 250µm/year. At the two Aarhus sites and at Lienz, localised corrosion was only found at one of the three samplings.

As a general trend, the localised corrosion started out relatively high and dropped accordingly at the last two samplings.

The only two sites to experience a localised corrosion rate above 100µm/year at the third sampling were Stockholm - Hässelby and Budapest. The rate at these two particular samples were even underestimated due to the fact that it was difficult to locate any original reference surface.

The pitting factor is not surprisingly very high for samples with hardly any corrosion besides a small pit. In such a case the high pitting factor truly indicates that the majority of the corrosion is in the form of pits. This seems to be the case for most of the plants in the beginning of the survey. At Budapest, however, the pitting factor starts at and stays at a low value indicating that the corrosion primarily is general with a maximum local corrosion rate that is only ten times larger than the general rate.

The two Stockholm sites, Southampton and to some extent Helsinki, start out with a high pitting factor indicating primarily localised corrosion but end up with a low pitting factor below 10 at the third sampling, indicating either that the pitting corrosion has been taken over by general corrosion or that the pitting corrosion has spread throughout the surface. The more pits on the surface, the lower the pitting factor gets due to the increase in weight loss.

At Děčín and Lemgo the pitting factor is rather stable around 20-30, which could be seen as an indication that the corrosion does not change but progresses with the same ratio. One explanation could be that the number of pits does not change significantly, but they grow in size and depth. This does however not comply with observations of the coupons. Instead it seems that the number of pits increase. Thus, the constant pitting factor could instead indicate that pits stop to grow at a certain size/depth and that new pits form.

Based on an overall corrosion evaluation, the two Aarhus sites and the site in Lienz do not experience a significant level of corrosion, which in terms is the effect of MIC. The plants: Lemgo, Helsinki, and Děčín are somewhat affected by corrosion, while the remaining: Stockholm - Hässelby, Budapest, and Southampton are more heavily corroded.

MIC or non-MIC
The question is now whether or not the observed corrosion is influenced by the presence of bacteria or not.

The level of biofouling points at Stockholm - Hässelby, Budapest, Lemgo, Southampton and to some extent Děčín.

Presence of sulphide and SRB indicate that the probability of MIC is low at Aarhus - Transmission, Helsinki, Lienz, and Stockholm - Värtan.

Looking at the corrosion, which is the main reason for worrying about MIC, Lemgo, Helsinki, and Děčín and particularly Stockholm - Hässelby, Budapest, and Southampton are relevant.

The sum off all indicators thus points at the following plants as having a high probability for MIC:

- Stockholm - Hässelby
- Budapest
- Lemgo
- Southampton

Stockholm - Värtan and Děčín are showing minor signs of MIC, while the two plants in Aarhus and the ones in Lienz and Helsinki show no sign of MIC.

Including the visual interpretation of the samples in the evaluation the following may be suggested for the plants:

Aarhus (both sites)
- Very little corrosion that does not seem to accelerate
- A low amount of biofilm
- Presence of sulphides indicating a potential danger for MIC

Conclusion: **Non-MIC**

Stockholm - Hässelby
- Large amount of biofilm
- Large amount of corrosion products
- High general corrosion rate started as localised corrosion but spread to the entire surface
- Presence of sulphide
- Presence of SRB

Conclusion: Corrosion affected by oxygen and pH fluctuations and **possibly MIC**

Stockholm - Värtan
- Low amount of biofilm
- Thin layer of corrosion products
- No SRB detected
- Presence of sulphide

Conclusion: **Possibly MIC**

Budapest
- Large amount of corrosion products
- Large amount of cells
- Sulphide present
- SRB present

Conclusion: Corrosion mainly due to a relatively high oxygen concentration, fluctuating pH, and SRB - **Possibly MIC**

Lemgo
- Large amount of biofilm
- Relatively high local corrosion rate
- SRB present
- Corrosion underneath tubercles

Conclusion: **MIC**

Lienz
- Same as the two Aarhus sites

Conclusion: **Non-MIC**

Southampton
- Clear distribution between unaffected surface and tubercles/streaks
- SRB present
- Sulphide present
- Large amount of bacteria

Conclusion: **MIC**

Helsinki
- Very low concentration of cells
- Localised corrosion
- No SRB
- Sulphide present

Conclusion: **Non-MIC**

Děčín
- Small amount of corrosion products
- Increasing amount of biofilm
- Increasing localised corrosion
- SRB present

Conclusion: **Possibly initiating MIC**

Aarhus and Lienz clearly belong to the group: Non-MIC, while Lemgo and Southampton reside as MIC. The remaining sites are not clearly identified as either MIC or Non-MIC. The tool box for identifying MIC clearly needs to be expanded, which is why this project has tested a range of promising new methods (see chapter 6).

5 Evaluation of test methods

In the following the test methods used in the basic investigation are discussed. The methods are evaluated individually and compared when appropriate.

5.1 Exposure

The two types of exposure chambers used in this project are different in several ways. The level of simulation is most likely highest within the annular chamber, while the stagnant chamber is much simpler in construction and thus cheaper to install.

Pipe flow simulation
The high water velocity inside the annular chamber created by the rotating cylinder, forms an environment quite similar to the one at the inner surfaces of the district heating plant. Adjusting the rotation speed of the cylinder allows for simulation of various flow velocities. The velocity used in this project has been in the order of a few meters per second. The water flow through the chamber needs only to be a few litres per hour in order to prevent growth of bacteria in the water phase of the chamber. This means that if the effluent from the chamber has to be discarded the continuous flow to the drain may be kept to a minimum. The effluent may have to be discarded due to either difficulties of returning the water to the system or due to the addition of chemicals to the water inside the chamber.

Besides the price of installation another drawback is the price for new coupons. In order to prevent corrosion on the back of the exposed mild steel coupons, these have to be coated. The present type of coating is Diamond Like Carbon (DLC) which may be quite expensive. The slightly rounded shape of the coupons may cause problems with some of the more special analytical techniques.

Stagnant water
The chamber used by the Swedish Corrosion Institute has previously been used in a project on corrosion in district cooling installations, with promising results. However, the present results points out that the exposure method may have problems with the level of simulation. The water velocity inside the chamber is only a few cm per minute. Thus, the chamber simulates flow conditions as found in dead ends or in large tanks. Furthermore, the combination of an incubation cylinder made of PVC with a long hydraulic retention time (1-2 hours) could cause the oxygen concentration in the chamber to rise. However, the results produced in this project do not show increased amounts of oxygen corrosion in these units. The corrosion rate in the stagnant water chamber is generally lower than the rate in the pipe flow simulation chamber apart from the plant in Budapest.

It is difficult to evaluate the effect of the stagnant water chamber on the amount of biofilm formed on the coupons. A direct comparison of the influence of the two different chamber types is not possible because bacterial numbers have been determined by different methods that are not directly comparable.

With respect to corrosion measurements it is important that the coupons used are cylindrical with a rather small radius and exposed on the outer side. This makes it virtually impossible to perform other corrosion analysis than weight loss and visual inspection.

5.2 Corrosion measurements

Figure 5.1 Graphic comparison of general corrosion rates as obtained using two different exposure methods.

Figure 5.2 Enlargement of the graph in figure 5.1 showing values below 5 micrometer/year

Two different methods (see above) were used to expose two different sets of corrosion coupons within the ten DH plants.

Coupons within the flowing water unit were produced of sheet metal and rounded to fit the inner surface of the exposure chamber (100mm in diameter). The back of the mild steel coupons were chemically isolated with a DLC coating. Thus the corrosion did only take place at the coupon surface facing the water flow.

Coupons within the stagnant water unit were produced as sections of pipe material, joined together endwise so only the outer surface was exposed. The exposed surface had a curvature radius of approximately 12mm.

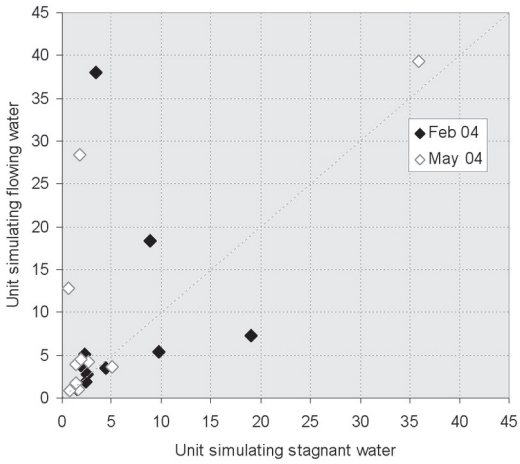
Looking at the data for general corrosion rates obtained using the two approaches, it may be noted that only in a about half of the cases there is agreement between the two (see figure 5.1 and 5.2). In two cases the corrosion rate measured within the stagnant water unit was higher than in the flowing water unit. In the remaining cases where the two results differed the rate was highest within the flowing water unit. Due to the coupon form in the stagnant unit, it was not possible to measure the local corrosion rate.

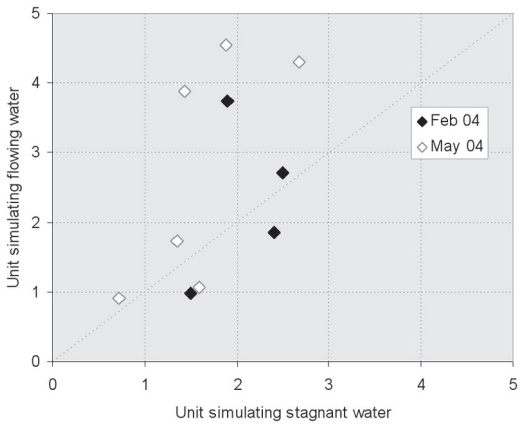
The difference between the two approaches are thought to be caused by:

1) differences in flow velocity within the units
2) differences in oxygen concentration due to oxygen penetrating the materials used for constructing the stagnant water unit

The low flow velocity within the stagnant water unit could cause the corrosion rate to either increase or decrease due to the low level of mass transport to and from the surface: if the corrosion is influenced by a biofilm acidifying the surface region, the low flow velocity may increase the effect. On the other hand, if the corrosion is limited by oxygen diffusion to the surface, the low flow rate may lower the corrosion rate.

In terms of biofouling, one may speculate that the low flow velocity yields thicker biofilms since the overall drag on the film is negligible. On the other hand, the flux of nutrients to the surface, being lower compared to the flowing water unit, may cause a reduction in biofilm accumulation within the stagnant water unit.





Oxygen penetrating the materials used to construct the stagnant water unit is thought to increase the corrosion rate. However the magnitude of the change is not known. The low flow rate within the unit again is assumed to lower the effect of oxygen.

Looking at the results again with this in mind it is surprising how many data points that correlate. The few cases where the rate within the stagnant water unit is significantly higher than in the flowing unit, are cases where the corrosion rate within the flowing unit is low. This may be an indication that in these cases the corrosion rate may be influenced significantly by the addition of small amounts of oxygen, which is normally the case in very clean systems with little or no magnetite.

In general the flowing water unit is believed to simulate the actual situation within the distribution system the best, by keeping an anaerobic environment and keeping the flow velocity up. This unit is thus believed to give the most reliable results, regardless of the nature of the corrosion processes.

5.3 Microbiological methods

Total bacterial counts
Two basically different techniques have been used to address the total number of biofilm cells on the corrosion coupons.

On the stagnant water coupons, the biofilm was removed by sonication in system water. A drop of the system water containing the loosened biofilm cells among others was placed between two glass slides at a fixed distance (0.1 mm). Through light microscopy of the slides the number of cells within a 500x500 µm area was counted at 400x magnification.

In order to see one cell within the selected area, the concentration of cells within the water has to be at least $4 \cdot 10^6$ cells/ml. By counting the cells within ten selected fields the theoretical detection limit may be decreased to $4 \cdot 10^5$ cells/ml. The detection limit for biofilm cells based on loosening 17 cm^2 biofilm in 55 ml system water is slightly higher $1.2 \cdot 10^7$ cells/cm^2.

The other method for total bacterial counts which was used on coupons from the flowing water unit was caried out according to [American Public Health Association/American Water Works Association/Water Environment Federation, 1995]. Briefly, biofilm cells were scraped off into filter sterilised water and a suitable amount was transferred to a 0.2µm filter. The cells were then stained with DAPI and counted using epi-fluorescense microscopy. Ten 100x100µm fields were counted at 630x or 1000x magnification.

Using the same approach for the detection limit as above, this method can detect about $4 \cdot 10^1$ cells/cm^2 provided all water is filtered and only one cell in one of the ten fields is detected. According to the standard an average of 40 cells should be counted within each field. This yields a detection limit of about $1 \cdot 10^4$ cells/cm^2.

Another basic difference between these two methods is that the cells in the first one are not fixed and will thus move around in between the two glass slides. Assuming that the thickness of the optical focus layer at the 40x objective covers the entire chamber thickness cells can only move in and out at the edges of the field. If the focus thickness is less than the thickness of the chamber, cells may move in and out of focus all over the field by moving upwards or downwards. The accuracy of the method when the cell number exceeds 100 times the detection limit (an average of 10 cells counted in each field) is therefore questionable.

Counting live and unstained bacteria using a 40x objective is a challenge even with pure cell cultures. It becomes very difficult when the sample contains other particles of approximately the same size like e.g. magnetite or sand/clay particles, which may seriously influence the results of the counting.

The used improved Neubauer chamber is developed for counting of sperm cells or blood cells. These type of cells tend to be almost an order of magnitude larger in diameter than bacteria. Thus, the use of a magnification of just 400x as prescribed for the improved Neubauer chamber could cause a problem with detection of bacteria.

The staining method is also influenced by particles within the sample. A high concentration of abiotic particles may limit the maximum amount of filtered sample because particle build up on the filter may block the view of cells underneath. Once the bacteria are killed and stained, the operator may clearly distinguish between intact cells and abiotic particles using either a 63x or a 100x objective. The only thing that may seriously influence the staining technique is autofluorescence of oily substances in the sample. However, none of the samples investigated in this study contained such matter.

Looking at the results from the two methods as applied to biofilm samples from the two exposure units, shows that they are not comparable (see figure 5.3). While the DAPI staining method reveals concentrations of biofilm cells ranging from 10^3 to 10^7 cells/cm^2, the counting chamber method only yields cell numbers around 10^8 cells/cm^2. Besides, there does not seem to be any correlation between the two data sets.

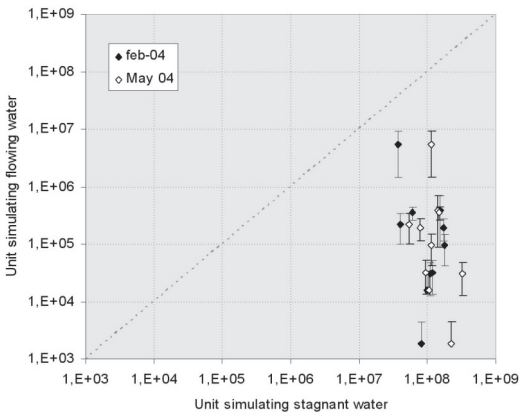


Figure 5.3 Comparison of total biofilm population obtained by two different approaches on coupons from the two units.

One explanation could be that oxygen penetrating the stagnant water chamber increases the biofilm population to a maximum value around 10^8 cells/cm^2. However, the corrosion data from this chamber does not seem to be influenced by oxygen.

Growth dependent enumeration of microorganisms

Of the worlds total population of bacteria, it is widely accepted that only a very small fraction (a few percent) are culturable, meaning that they will continue to reproduce once they are removed from their natural habitat and transferred to an artificial growth medium. With this in mind all growth based techniques suffer from a lack of correlation with the original sample. In some cases though, particularly within the food production industry, the artificial media may be engineered to match the natural environment so good that an acceptable correlation may be achieved. In most other cases no information on the correlation exist.

The methods used in this study follows standard methods for most probable number techniques. Some have even been improved according to the latest knowledge on specific organisms. Some of the late studies in Danish DH systems do however point out that there is little or no correlation between growth based techniques and non growth based techniques in DH waters.

Compared to the total number of bacteria measured on coupons from the stagnant water unit, the sums of results of the incubations of agar plates applied to the same samples only account for 0.1-1‰ of the total population.

Thus, even though the MPN methods show different results for the ten plants, an evaluation of the biological activity based on less than one ‰ of the population would be questionable.

On the other hand incubations on agar plates can give valuable qualitative information such as the surprising presence of eutrophic, heterotrophic, aerobic bacteria in all investigated DH plants.

Sulphate reduction

The identification of sulphate reducing bacteria in terms of detecting their production of sulphide in a specific growth medium has been used extensively during the past years investigation of MIC in Danish DH systems. Not because the method was particularly accurate and quantitative, but because it was the best available technique at the moment.

Both the Swedish MPN incubations and the Danish detection of produced H_2S are based on the detection of activity of SRB. They lack a direct connection to the real population just as the above mentioned methods based on agar plates, because the sulphate reducing bacteria have to be able to grow and/or metabolise within the medium. Otherwise no signal is observed.

In this study, positive sulphide reduction was only identified in two cases of biofilm on stainless steel using the Danish approach, while on 9 of 20 occasions very low numbers of SRB (0,2-5 per cm^2) were found using the Swedish MPN-technique. Compared to the identification of sulphide minerals, which was positive to some extent on all samples, one may doubt the results for sulphate reduction. In district heating systems, the only possible explanation for sulphide minerals is microbiological reduction of sulphate.

6 Test of complex methods for further evaluation of MIC

As part of the project a number of relatively new techniques which have proven to be of great use in other systems have been tested on exposed coupons. The reason to do so was basically a wish to create a tool box of methods usable to distinguish between MIC and non-MIC.

The new techniques were chosen within the areas of: surface chemistry, surface electrochemistry and molecular biology. The following methods have been tested:

- Energy dispersive X-ray fluorescence (EDXRF) for analysis of elemental composition of scale and corrosion products on the surface of exposed coupons.
- Small spot EDXRF for mapping of element distribution on the surface, particularly in the vicinity of localised corrosion attacks.
- Fluorescent in-situ hybridisation (FISH) for direct detection of specific bacterial groups within deposits and corrosion tubercles.
- Localised electrochemical impedance spectroscopy (LEIS) as a tool to measure corrosion processes directly on the surface.
- Scanning kelvin probe to map corrosion potentials across the surface.

These methods have primarily been tested on coupons exposed in the four Aarhus and Stockholm sites in order to have as fresh samples as possible to work with. All tests have been performed using coupons exposed in the flowing water unit.

In the case where the tests showed positive results in terms of usability of the methods, additional analysis have been performed on interesting samples from the other plants.

6.1 Surface chemistry

To get a better idea of the nature of the corrosion occurring on the exposed coupons, the chemical composition has been analysed either as an average covering a larger area of the surface or as distribution across the surface. The idea was to find out if there was a particular distribution of elements around sites of localised corrosion.

Elemental composition
Chemical composition of deposits formed on the exposed coupons have been addressed using EDXRF.

Energy dispersive X-Ray fluorescence (EDXRF) is a fast technique for elemental analysis of solid materials. The technique is based on the samples being irradiated by X-Rays from a radiation source and subsequently emitting an X-ray fluorescent signal that can be detected. The elements and their concentration are identified by counting the pulses at the different energy levels. Usually a multi channel analyser is used for display and providing the data. Here each channel counts the number of photons with a certain energy level simultaneously. The resolution of an EDXRF spectrometer improves at higher energy levels but it also depends strongly upon the detector used.

Results
Spots of local deposits which were assumed to have localised corrosion attacks underneath were analysed. The presence of corrosion was verified after analysis. Figures show the X-ray spectrum for each sample.

Lemgo
A small line of deposit was analysed and found to consist of the following elements given in atomic percent:

Element	At%
Al	1.94
Si	2.17
P	0.61
S	0.81
Ca	0.05
Fe	94.42

Particularly the simultaneous presence of sulphur and phosphorous does in this case indicate that the corrosion may be MIC. The content of aluminium and silicon may in this case originate from clay/soil traces in the feed water.

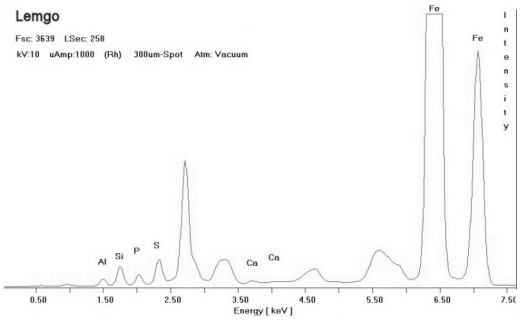


Figure 6.1 X-ray diffraction curve obtained from a carbon steel coupon exposed in Lemgo

Stockholm, Värtan
A relatively thick layer of deposit was analysed and found to contain the following elements:

Element	At%
Cu	6.93
Al	0.64
Si	0.52
P	0.08
S	9.15
Fe	82.67

In this case the sulphur content is very high. The collected signal will contain a portion of the base metal underneath the deposit, which is why the iron content in these analysis is so high. The sulphur content of nearly 10% may therefore be significantly higher within the deposit itself. Spot tests for sulphide have shown that the sulphur or at least some of it is in the form of sulphides, presumably iron and copper sulphides. The high concentration of copper may originate from corrosion of copper and brass components within the particular system.

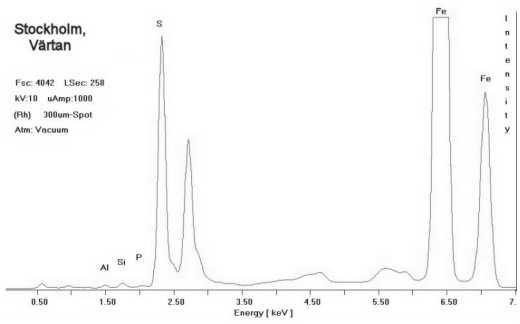


Figure 6.2 X-ray diffraction curve obtained from a carbon steel coupon exposed in Värtan

Stockholm, Hässelby
A large tubercle (several mm across) has been analysed and found to contain the following elements:

Element	At%
Si	3.05
S	8.27
Ca	1.98
Fe	84.75
Cu	1.96

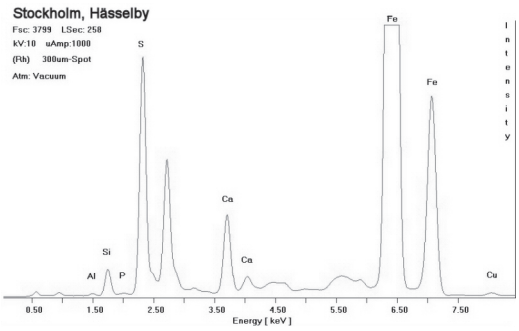


Figure 6.3 X-ray diffraction curve obtained from a carbon steel coupon exposed in Hässelby

The composition is similar to that found on the coupon from Stockholm, Värtan. The copper content is however a bit lower and there is far more silicon (clay/sand particles) present.

Décin
A small line of deposit was analysed and found to consist of the following elements given in atomic percent:

Element	At%
Al	0.62
Si	8.55
P	0.53
S	3.66
Ca	0.04
Fe	86.59

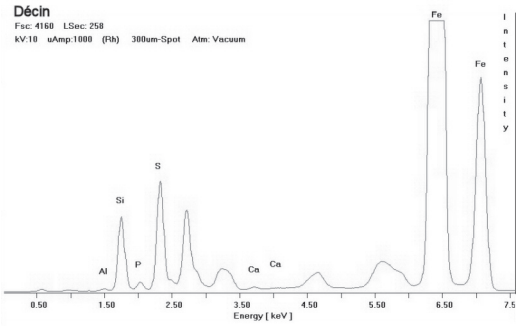


Figure 6.5 X-ray diffraction curve obtained from a carbon steel coupon exposed in Děčín

The presence of silica and aluminium again may originate from clay/sand minerals, whereas the presence of sulphur combined with a positive spot test for sulphide must be more or less in the form of iron sulphides. Also the simultaneous presence of phosphorous points towards action of MIC.

Southampton
A larger streak of deposit was analysed and found to consist of the following elements given in atomic percent:

Element	At%
Al	7.10
Si	6.42
P	0.51
S	3.61
Ca	0.04
Fe	79.21

The composition resembles what has been seen at the other local corrosion sites: sand/clay minerals, sulphide (determined by spot test) and phosphorous.

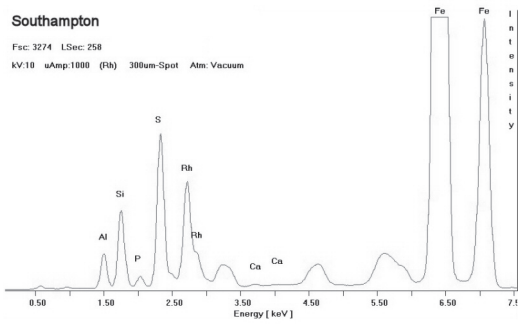


Figure 6.4 X-ray diffraction curve obtained from a carbon steel coupon exposed in Southampton

Mapping
An additional software package, allows the analyst to acquire and save spectral data at each and every pixel in a selected area. It is thus possible to analyse the elemental distribution throughout a chosen area and create images of each present element. Using an option for saving complete spectra at every pixel, it is not necessary to define all the elements which need to be mapped. Afterwards, spectral data can be retrieved and used to generate single or composite spectra, line scans or elemental maps. The mapping software creates a database that correlates the spectrum at each map pixel with the corresponding position in the mapped video image or in an elemental map.

Results

Stockholm - Hässelby
Mapping of a corroded area on one of the coupons exposed in the Stockholm - Hässelby network showed a rather uniform distribution of silicon, copper and calcium. Sulphur was not uniformly distributed but was concentrated in more dense areas. The signal for iron was somewhat depleted in isolated areas.

Cleaning off the scale and corrosion products on the surface revealed localised corrosion attacks at points of elevated sulphur content.

It is believed that within the relatively thick layer of corrosion products that were found on the Hässelby coupons, sulphate reducing bacteria among others were active in localised areas causing localised corrosion.

Děčín
Only smaller spots of deposit/scale were found on the Děčín coupons. These spots contained mainly iron, silicon and phosphorous with traces of sulphur. The spots were associated with localised corrosion attacks underneath.

It is believed that these spots may be a preliminary sign of MIC. The processes are not clear enough to give a more precise description based on the mapping.

Lemgo
The coupons from the Lemgo network looked similar to the coupons from Děčín. The spots of corrosion products were though larger in both thickness and size. Calcium, phosphorous and sulphur, the three most abundant elements besides iron on the coupon surfaces were somewhat concentrated around the spots. Particularly sulphur seemed primarily to be present within the spots.

The coupons from both Děčín and Lemgo were characteristic in the way that the surface was only covered with deposits in defined areas/spots. The surface area in between the spots were practically free of deposits.

Stockholm - Värtan
Deposits from the Värtan coupons were quite thick and porous in nature. Mapping the depos-

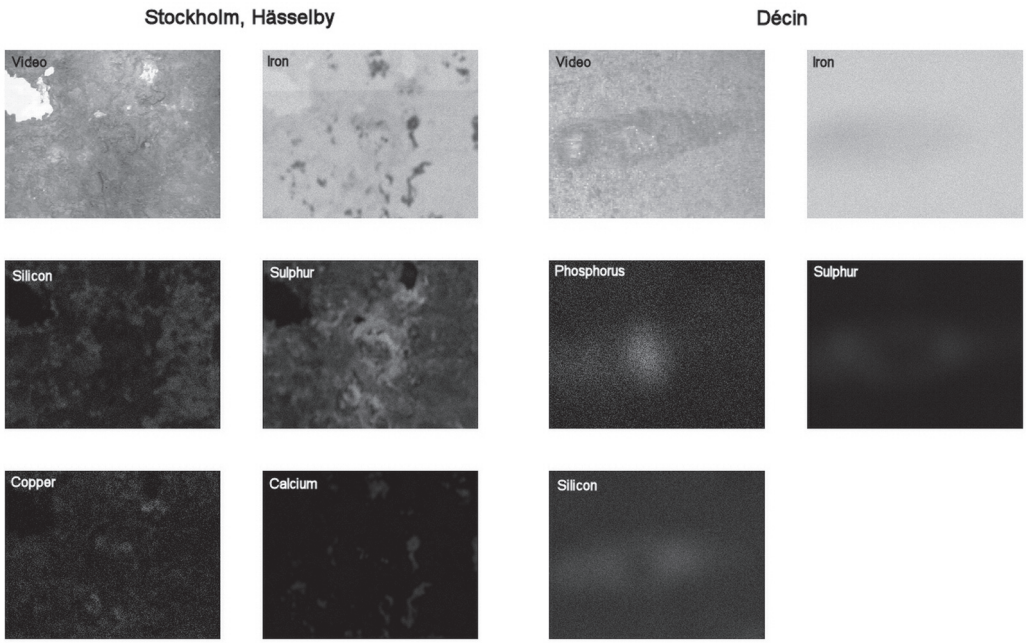


Figure 6.6 X-ray diffraction map obtained from a carbon steel coupon exposed in Hässelby (left)

Figure 6.7 *X-ray diffraction map obtained from a carbon steel coupon exposed in Děčín (right)*

Figure 6.8 *X-ray diffraction map obtained from a carbon steel coupon exposed in Lemgo (left)*

Figure 6.9 *X-ray diffraction map obtained from a carbon steel coupon exposed in Värtan (right)*

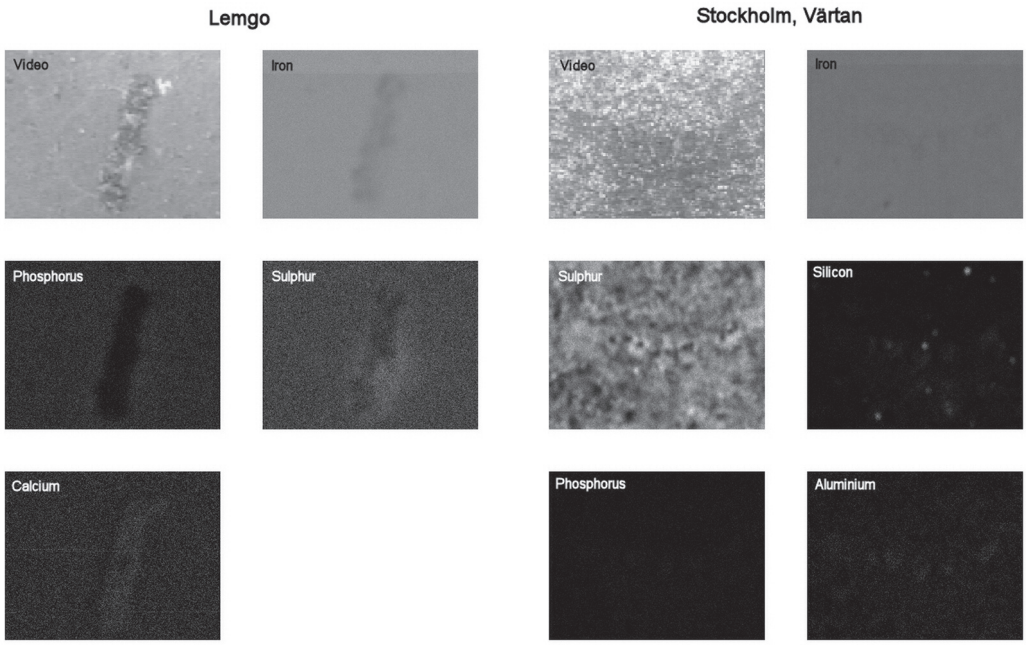
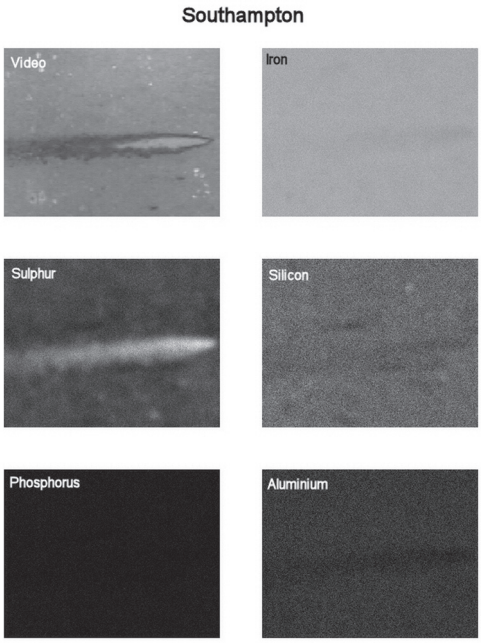


Figure 6.10 *X-ray diffraction map obtained from a carbon steel coupon exposed in Southampton*



its for elements only revealed a rather homogeneous layer of iron and sulphur with smaller traces of phosphorous, silicon and aluminium. In this case sulphate reducing bacteria are assumed to be active throughout the entire deposit, creating a mixed layer of iron oxides and iron sulphide.

Southampton

On the surface of the Southampton coupons the deposits were concentrated within elongated spots or streaks, which in shape resembled a meteor with a dense head and a lesser dense tail. Sulphur was the only element to follow the shape of the streaks, as the highest concentration of sulphur was located at the dense end and decreased within the tail.

Silicon, phosphorous and aluminium also found on the surface were more homogeneously distributed.

This type of deposit is typical for MIC as it starts at a point and spreads downstream as the bacteria reproduce and the tubercle created starts leaking.

6.2 Molecular biology

Figure 6.11 DAPI staining of bacteria directly on the surface of a coupon exposed in the Southampton plant

Fluorescent in-situ hybridisation
Fluorescent in-situ hybridisation (FISH) as a tool to directly distinguish between different groups of bacteria without any incubation steps, was tested on coupons originating from Aarhus - transmission and Stockholm - Hässelby. FISH is used in the same way as DAPI staining as used to perform direct count of the total bacterial population on the coupons. However, FISH targets a group of active bacteria, either all active eubacteria or more specific groups like deltaproteobacteria which includes several strains of sulphate reducing bacteria. The method was tested on both mild steel and stainless steel.

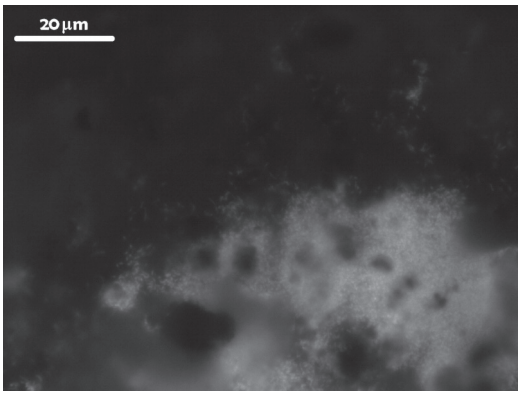
Molecular biology methods
Fluorescence in situ hybridisation was performed with 16S fluorescently labelled rRNA-targeted nucleic acid probes (Thermo Hybaid, Ulm Germany) on biofilm samples [Amann et al., 1995]. Samples were fixed in fresh 4% (W/V) paraformaldehyde or 50% ethanol (V/V), washed 3 times in filtered distilled water, stained with DAPI (1 mg·ml^{-1}), immobilised on slides (Marienfeld), and hybridised. The filter sets 09 and 10 (Zeiss) were used for microscopic examination and 100x magnification objective for oil was used. CY3 labelled specific probes were used for enumeration [Bouvier, 2003].

The following probes were used:

- Generally active eubacteria - EUB338-mix (I+II+III)
- Sulphate reducing bacteria - SRB385 (Deltaproteobacteria)

Results
Despite our effort in using FISH directly on the surface of the coupons, it was not possible to obtain a clear signal. DAPI staining followed by microscopy could be performed directly on the surface though and was carried out on the surface of stainless steel coupons from Southampton (see figure 6.11).

Instead biofilm/deposits were scraped from the surface, suspended in sterile water and transferred to a filter. The same method was used in the total counts performed. In this case it was possible to get a clear FISH signal from the stained bacteria. Even small amounts of corrosion products did however disturb the method in such a way that it was impossible to distinguish individual bacteria.



Thus it was only possible to obtain reasonably good results on biofilm scraped from stainless steel coupons (see figure 6.12 and 6.13)

On these samples, good indications of active eubacteria was found as a large part of the cells stained by DAPI also turned out as positive using the FISH stain for general eubacteria. The samples from Stockholm contained auto fluorescent particles or particles that adsorbed the FISH stain. Thus it was not possible to obtain a clear FISH signal from these coupons (see figure 6.14 and 6.15).

None of the coupons which were possible to analyse using the FISH technique showed any positive signals using the probe for sulphate reducing bacteria (delta proteobacteria). In pre-

Figure 6.12 microscope image of DAPI stained biofilm cells scraped of a stainless steel coupon from Aarhus - transmission

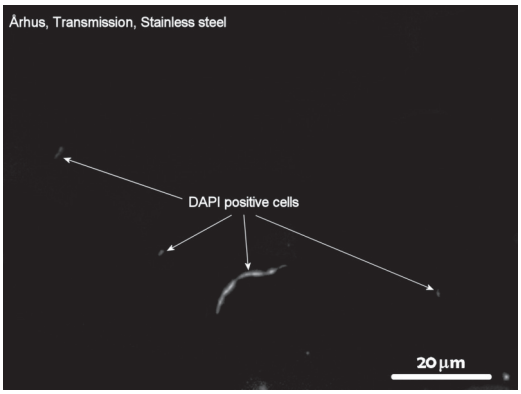
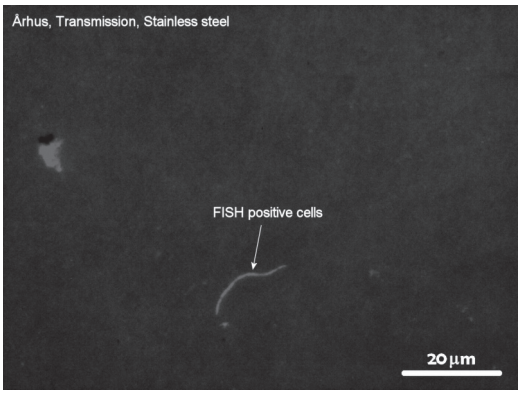


Figure 6.13 same immage as figure 6.12 but with the fluorescent FISH signal for general eubacteria lightened up. Note that not all the cells showing a positive DAPI signal (figure 6.12) show a positive FISH sgnal too.



vious studies of fouling in district heating systems in Denmark positive presence of SRB has though been shown using this probe.

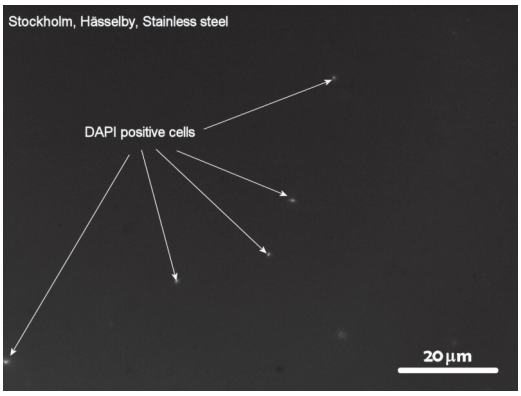


Figure 6.14 microscope image of DAPI stained biofilm cells scraped of a stainless steel coupon from Stockholm - Hässelby

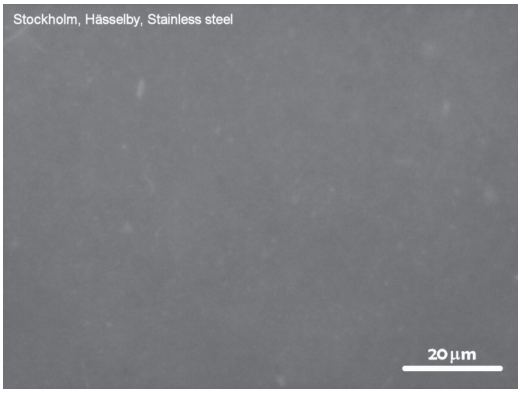


Figure 6.15 same image as figure 6.14 but with the fluorescent FISH signal for general eubacteria lightened up. Note that the image is dominated by unspecific binding of the FISH probe to the sample and that individual cells do not show.

6.3 Localised Electrochemical Techniques

Any material that is exposed to a suitable environment will sooner or later be colonised by microorganisms, such as bacteria, fungi and algae. The microorganisms will form colonies of their own kind and change their immediate surrounding to their needs, e.g., some species of Thiobacillus will reduce the pH to values below 2. Such colonies are ranging from a few µm to several 100µm in size. Since several different species are colonising the result is a heterogeneous biofilm with several different chemical environments in close approximation to each other. Conventional microscopic and electrochemical techniques can not be used to study the localised mechanisms on the surface, since sample preparation will change the surface and conventional electrodes are normally in the mm2 or cm2 range. Environmental scanning electron microscopes and scanning probe microscopes overcome the need for sample preparations and localised electrochemical techniques, such as scanning reference electrode technique, scanning vibrating electrode technique and localised electrochemical impedance spectroscopy, have been successfully applied for studying localised corrosion in the past. This part of the project aims to investigate if Scanning Probe Techniques, such as Scanning Vibrating Electrode Technique (SVET) and Local Impedance Spectroscopy (LEIS) are suitable techniques for the detection of MIC in district heating systems.

Localised electrochemical methods

Variations in electrochemical properties, such as potential and current, across metal surfaces, which may be related to localized attacks, have been demonstrated many times. Evans [Evans, 1949; Thornhil and Evans, 1938; Evans and Agar, 1960] published the earliest reports, and other contemporary work was carried out by Jaenicke [Jaenicke, 1943; Jaenicke and Bonhoeffer, 1944]. These studies involved macroscopic bimetallic couples of zinc and steel. Equipotential and ion flux lines were determined in the adjacent electrolyte using manually movable reference electrodes in combination with Luggin capillaries. Various attempts were subsequently made to construct instruments to measure localized activity over samples that were not necessarily macroscopic bimetallic couples. The progress of these developments was periodically reviewed [Budd and Booth, 1965; Gainer and Wallwork, 1975].

The Scanning Reference Electrode Technique (SRET) was applied by Isaacs. He used it to study pitting and intergranular corrosion on stainless steels [Isaacs and Vyas, 1981]. Isaacs has also been closely associated with other innovative designs, notably the Scanning Vibrating Electrode Technique, SVET, in which the probe is mounted on a biomorph piezoelectric reed that vibrates the tip normal to the electrode at a characteristic frequency [Jaffe and Nuticelli, 1974]. SVET has been used to investigate the initiation of stress corrosion cracking [Isaacs, 1988], surface heterogeneities [Isaacs, 1987], precipitation in aged duplex stainless steels [Jiang et al., 1992], and edge behaviours of painted galvanized steel plate [Zou et al., 1995]. A variation of this technique has been used in localized measurements of Electrochemical Impedance Spectra (LEIS) [Isaacs and Kendig, 1980; Lillard et al., 1992; Bayet et al., 1997].

The vibrating capacitor or Kelvin technique [Lord Kelvin, 1998], which has been used for a long time to measure the work function or contact potential of metals in vacuum or in gases and to study the adsorption of species on the surfaces of metals [Zisman, 1932; Hackerman

Table 6.1 Summary of localised electrochemical techniques and their resolution.

Technique	Description	Spatial Resolution
Scanning Reference Electrode Technique (SRET)	Measurements of current density or potential distribution over the surface scanned in a solution	~20 µm
Scanning Vibrating Electrode Technique (SVET)	Measurements of DC current density distribution over the surface scanned in a solution	15 µm
Localized Electrochemical Impedance Spectroscopy (LEIS)	Measurements of ac current density distribution over the surface and local impedance spectra in a solution	20 µm
Scanning Electrochemical Microscopy (SECM)	Measurements of local oxidation-reduction current in a solution	20 nm
Scanning Kelvin Probe Microscopy (SKPM)	Measurements of potential or work function distribution over a surface in atmosphere	5 µm
Scanning Kelvin Force Microscopy (SKFM)	Measurements of potential or work function distribution over a surface in atmosphere	20 nm

and Lee, 1955; Mundt and Benndorf, 1993], has been adapted to the measurement of corrosion potential [Stratmann, 1987]. Stratmann and his co-workers have applied Kelvin probe method to study the atmospheric corrosion of metals covered with thin electrolyte layers [Stratmann and Streckel, 1990a; Stratmann and Streckel, 1990b; Stratmann et al., 1990]. In 1991, a scanning Kelvin microprobe system was described [Yee et al., 1991]. Since then, the Scanning Kelvin Probe Microscope (SKPM) has been successfully used in corrosion science, especially for mapping the potential distribution under organic coatings [Stratmann et al. 1991]. A further development of this technique was the application of a vibrating conductive Atomic Force Microscopy (AFF) cantilever to measure the work function on surfaces at for AFM typical lateral resolutions of 20 nm (Electromagnetic Force Microscopy (EFM) or Scanning Kelvin Force Microscopy (SKFM)).

Scanning Reference Electrode Technique (SRET)

The corrosion of metal in an electrolyte is an electrochemical process involving an anodic oxidation of the metal and a cathodic reduction of species in the solution. During localized corrosion, the two processes usually take place at well-separated areas. The flow of electrons within the metallic phase does not involve significant ohmic potential differences because of the high conductivity of the metal. The flow of current within the liquid phase is associated with small potential changes between the anodic and cathodic areas. By scanning a "passive" reference probe electrode, the potential distribution in the liquid can be measured. Thus the SRET is an in-situ technique used to locate the anodic and cathodic sites and to study the electrochemical processes during localized corrosion without altering the processes taking place, changing the local environment over the corrosion site, or influencing the rate of corrosion. Isaacs and Vyas (1981) have reviewed the applications of SRET, including pitting corrosion, intergranular corrosion, welds and stress-corrosion cracking.

Scanning Vibrating Electrode Technique (SVET)

The SVET technique measures a dc-current flowing over a metal surface as a consequence of the separation of anodic and cathodic sites during corrosion. The technique is a modification of SRET and overcomes the problem arising from background noise. Vibrating the tip of a microelectrode in a potential gradient converts the dc-potential variation associated with the current flow to an alternating current (ac) -signal with one specific frequency for one-dimensional vibration [Isaacs et al., 1996] or two specific frequencies for two-dimension of vibration. This allows better amplification of the signal and filtering of background noise. An additional advantage of SVET is that the probe can be vibrated in more than one direction. If it is simultaneously vibrated in two perpendicular directions with different frequencies, then the magnitude of the electric field in the two direc-

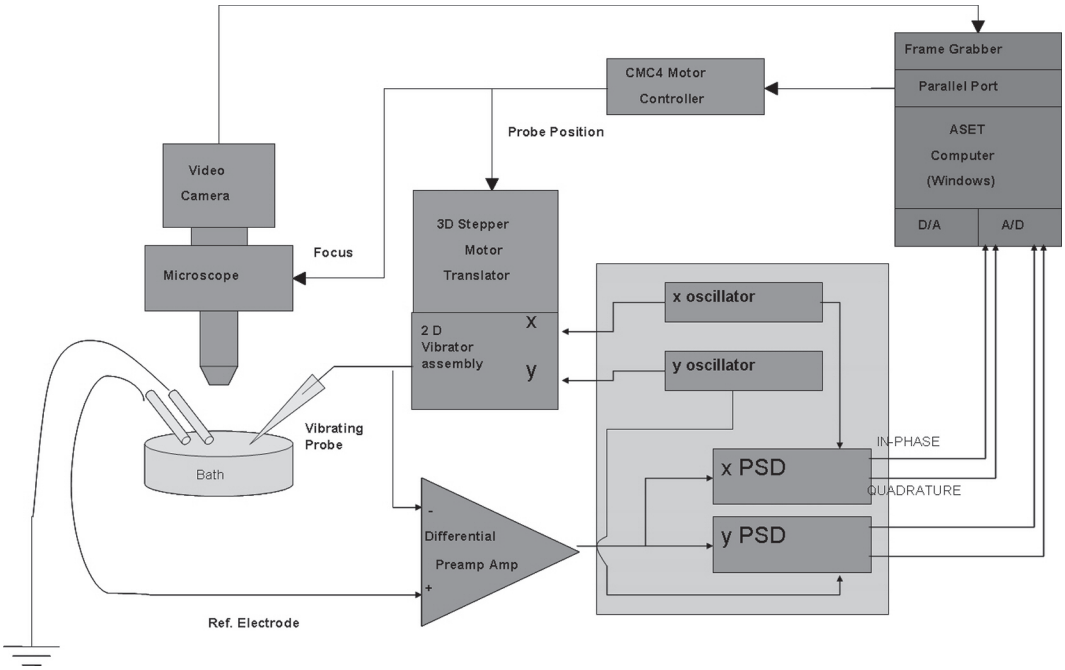


Figure 6.16 Overview of the SVET design.

tions can be determined by the use of two lock-in amplifiers, each tuned to the frequency of one of the two vibration directions [Davenport et al., 1992].

SVET has been applied to pitting corrosion studies in the presence of bacteria [Franklin et al., 1991], crevice corrosion of stainless steels [Isaacs and Ishikawa, 1985], corrosion fatigue of high strength steels [Fujimoto et al., 1990], local polarisation curves [Jiang et al., 1992], defects of organic coatings [Isaacs et al., 1996], degradation of coated metals at edges [Zou et al., 1995], corrosion inhibitors [Davenport et al., 1992; cheffey, 1988], and microbial corrosion [Mollica et al., 1997].

Localized Electrochemical Impedance Spectroscope (LEIS)
Electrochemical Impedance Spectroscopy (EIS) has been used extensively to study the corrosion phenomenon. However, the interpretation of the data is generally difficult due to the complexity of the systems studied and to the fact that impedance data is averaged over the whole exposed area while the corrosion generally occurs locally. The contribution of the corrosion reactions to the overall impedance spectra may be difficult to separate. Several attempts to develop a scanning impedance technique have been reported in the literature. One technique used thin-layer cell geometry. The size of the probe was relatively large and limited the spatial resolution and any mass transport taking place [Isaacs and Kendig, 1980]. A novel method of measuring local impedance spectra was reported [Lillard et al., 1992], where a bi-electrode consisting of two isolated metal wires was used to measure the local current density. Another method was reported to perform local electrochemical impedance measurements by adaptation of the SVET to ac mode [Bayet et al., 1997].

LEIS has been applied for the study of pitting corrosion on stainless steels [Annergren et al., 1997] and the detection of heterogeneities in organic coatings [Wittman and Taylor, 1995; Lillard et al., 1995; Zou and Thierry, 1997].

Scanning Kelvin Probe Microscope (SKPM) and Scanning Kelvin Force Microscope (SKFM)
The Kelvin microprobe (KP) method is based on an audio-frequency current (or voltage) that drives an electromagnet (or piezo-electric actuator), and the vibrations are transmitted mechanically to a small probe mounted perpendicular to the surface of the specimen. The vibration of the probe causes a corresponding variation in the capacitance across the air gap, so that an alternating current is set up in the circuit [Yee et al., 1991]. A motorized X-Y stage controlled through a microcomputer is used to scan over the specimen. The KP potential is measured through an electronic feedback system that uses the ac-signal from the working electrode as a driving force for the control circuit. The ac-signal is first amplified and then sent to the lock-in amplifier. The output of the lock-in amplifier is then used to adjust a battery applied between the probe and the sample. Until the null condition is reached, the data are sent to the computer for display and analysis. Instead of using an integral feedback circuit, the linear regression method can be used to determine the KP potential [Zou, 1994]. The critical element of the SKPM experiment is the vibrating electrode. The probe is vibrated in the vertical direction either by a magnetic element or by a piezoelectric actuator. Various probes have been used such as Pt wire [Huang et al., 1991], Au-plated steel [Stratmann and Streckel, 1990a], Cr/Ni wire [Yee et al., 1991], Ag/AgCl wire [Atanasoski et al., 1994] and an electrochemical etched tungsten tip [Mäckel et al., 1993]. The smallest tip size reported is about few microns in diameter [Yee et al., 1991; Mäckel et al., 199].

The previous applications of the Kelvin probe method in corrosion science concern the atmospheric corrosion of metals covered by thin electrolyte layers [Stratmann and Streckel, 1990a; Stratmann and Streckel, 1990b; Stratmann et al., 1990]. The recently developed scanning Kelvin probe technique has been used to detect heterogeneities on the surfaces in various environmental conditions. The applications of SKPM are, e.g., the potential distribution under organic coatings [Yee et al., 1991; Stratmann et al., 1991], potential (or work function) topography on passive film of 316L stainless steel [Han and Mansfeld, 1997], and work function mapping of the surface of thin anodic TiO2 films grown on a Ti polycrystalline substrate [Huang et al., 1991].

The combination of AFM and Kelvin probe technology is a new powerful tool to obtain high-resolution maps of the surface potential distribution on conducting and non-conducting samples. This technique was applied to samples that have been abraded with an AFM tip [De-

Vecchio and Bhushan, 1998]. The authors could demonstrate that even at low loads (no wear scars could be observed), the potential distribution of the surface changed. The advantage of the technique is that one obtains a topographical image at the same time as the potential map, thus allowing comparison between topographical changes and changes in the potential distribution. The application of this technique for studying pitting, intermetallic and intergranular corrosion, and corrosion of electronic circuits is ideal.

Materials and methods

The SVET system applied to this study was supplied by Applicable Electronics, USA. The SVET can measure voltage gradients down to nV at a minimum speed of approximately 50 ms per scan point. Voltage gradients are not disturbed by the probe's vibrations, which are typically 200 Hz to 1 kHz. The 2D vibration is accomplished by use of piezoelectric wafers driven by sine wave oscillators. Scanning is done with a 3D stepper motor micromanipulator. The SVET system is also capable of Scanning Local Electrochemical Impedance

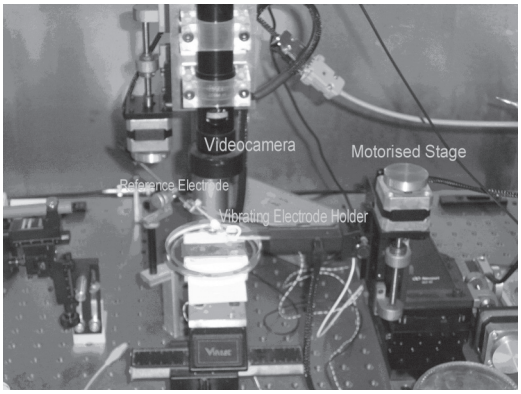


Figure 6.17: SVET setup

Spectroscopy (SLEIS) measurements. The SLEIS can measure below the 1.0 kHz range (typically 30-100 Hz). Essentially, one leaves the microelectrode stationary (non-vibrating) and then drives the sample with the oscillators in the PSD-2 amplifier, either directly, or via a potentiostat. Another mode is available as well to allow one axis to measure as an SVET and the other to measure as LEIS simultaneously while scanning the probe over a sample under potentiostat control. These methods of measurement provide the user with high sensitivity and a spatial resolution limited by the electrode tip, typically 5-50 µm diameter.

The software used to control the measurements was Science Wares' ASET software. This system is capable of automated voltage and current measurements in aqueous media.

The vibrator linkage is driven by two different signals from two separate sine/cosine oscillators. This moves the vibrating probe in a lissajous-like motion (overall square pattern made with two different frequencies). The linkage vibrates in two planes, one vertical and one horizontal (Perpendicular to sample and parallel to sample).

The vibrating electrode is electroplated with a Platinum Black tip. This plating makes the tip highly capacitive as a result of the large surface area created by the platinum black plating. If this tip is vibrated in an aqueous medium in the presence of an electric field it will detect a voltage drop across it's vibration distance. The platinum blacked electrode is like a single plate of a capacitor that is made up of this plate and the sample surface as the other plate. The bathing medium is the dielectric between those two plates. If one plate moves with respect to the other (probe) and there is a voltage on the other plate (sample) then charge distribution on these plates will change due to the distance between those plates, which is proportional to the potential of the sample.

Another analogy is to think of the corroding sample as a voltage source and the liquid medium as a resistor. The electrode is like the wiper arm of a potentiometer. As one moves the wiper arm back and forth along the resistive element, one will see a change in voltage from one end of the movement to the other. That change will occur at the same rate as the motion of the wiper arm. Since the probe is vibrating with a sine wave, the signal on the probe, in the presence of an electrical field, will be a sine wave that has the same frequency as the vibra-

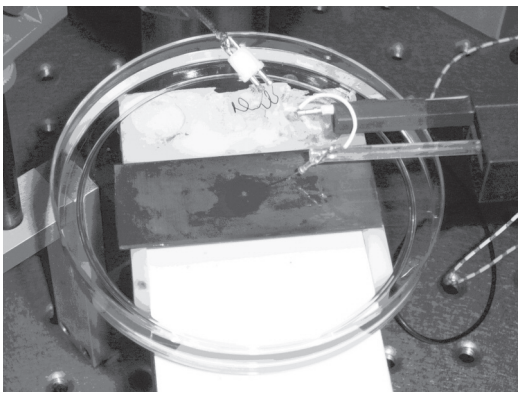


Figure 6.18: Sample, scanning tip and reference electrodes of the SVET system.

tion driver signal. Therefore, the vibration will develop an AC signal by a DC voltage gradient in the medium due to the Ohmic resistance of the solution. One must, however, vibrate parallel to the field lines to sense a potential difference from one end of the excursion to the other. The electrode signal is then amplified to a level that allows it to be processed electronically. The signal is then fed into phase sensitive detectors (PSD) along with a reference signal from the oscillators driving the vibrating electrode. If the electrode signal is the same frequency as the reference signal then it is detected. The phase offset is mostly due to mechanical lags in the system along with small electronic phase shifts. The software makes phase adjustments to compensate for these phase lags during calibration. The PSD then converts the probe's AC signal to a DC voltage that represents current density.

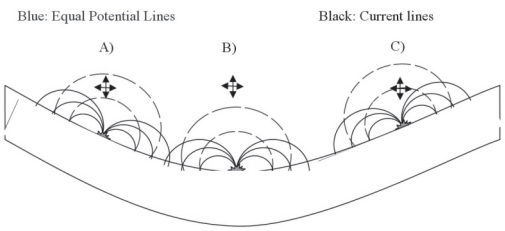


Figure 6.19 Demonstrating the difficulties in measuring current density maps on bend samples. A) The vibrating electrode (double arrow) is measuring at calibrated height above the sample in y and x direction; however the vector of the measurement is not 90 degrees to the surface, resulting in an error of the current vector direction. B) the measurement is performed at the right angel, however not at calibration height, resulting in an underestimation of the current density. C) The measurement is performed to close to the surface and the angel of vibration is not correct, resulting in an overestimation of the current density and wrong current vectors.

The system has two phase sensitive detectors (PSD-2). One marked X (typically horizontal current density) and the other Y (typically vertical current density). Both X and Y PSDs have an in-phase and quadrature output. The in-phase is intended to be that output which is maximum, when properly phased, while detecting a real signal. The quadrature is intended to be zero or minimum output when a real signal is detected. This means that the quadrature should have very little or no output when measuring a real current. The PSD signals are then output to the computer's A/D board. The ASET software calibrates the system and determines phase angle of the in-phase and quadrature outputs for the X and Y PSD amplifiers.

Results and discussion

As mentioned above, in order for the system to work, it is necessary to scan parallel to the sample surface at a constant distance between sample and the tip of the scanning electrode, commonly 150 µm. The samples received have a radius so that they fit into the rotating cylinder bioreactor that was used to create a known and reproducible sheer force on the sample surfaces. The generated AC-signal from the vibrating electrode as a function of the Ohmic drop, caused by the current density in the solution, is directly proportional to the spacing between electrode, and sample surface and resulting measurement errors due to the curvature of the sample could be compensated via relative simple calculations within small height changes. The other problem, the tilting of sample and therefore the shift in geometry of the current vectors that are arising from the curvature of the samples is not so easy to overcome as illustrated in figure 4. With increasing distance to the sample the sensitivity is reduces and spatial resolution is lost.

Several attempts were made to measure local currents on the surface of the samples received from district heating plants. Unfortunately, these attempts were not successful, since the curvature of the samples did not allow scanning sufficient large areas to detect localised corrosion and the tip crashed into the surface as shown in figure 5. The actual bending of the tip is not posing a problem, however, if the impact with the surface is strong enough that the tip is losing the deposited platinum, the electrode needs to be newly prepared and calibrated, a procedure taking ca. 45 minutes. Therefore, it was decided not to continue with SVET experiments as a tool to detect MIC in district heating plants.

In conclusion, the curvature of the samples was not allowing scanning larger areas than a few mm2 before the change in the probe-sample distance was changed by over 50% from its initial value, making it impossible to perform measurements that were meaningful (data not shown). It was not possible within the budget of this project to develop a mathematical model allowing compensating for geometrical effects of the samples on the measurements, such as deconvolution models. Since the biofilms are relatively small and heterogeneous, many measurements with calibration of the tip-sample distance for each location would be needed to be performed in the presence of an active biofilm and when the biofilm would be inactivated (non-oxidising biocide) in order to draw conclusions on the activity and influence of biofilms on the corrosion process in district heating systems.

Study of the metal surfaces covered by biofilms by Electrochemical Impedance Spectroscopy (EIS)

In EIS a small alternative current flow between working and counter electrode in water electrolyte. The sinusoidal changing in voltage, E (t), creates a response in the form of an alternative current, I(t). Impedance (Z) is the complex resistance of the electrochemical system to alternative current. The relation between E (t), I(t), Z and time is given by:

$$Z = E(t) / I(t) \quad (1)$$
$$E(t) = Eo \exp(jwt) \quad (2)$$
$$I(t) = Io \exp(jwt - Q) \quad (3)$$

where j is imaginary unit, w the frequency, Q the phase shift and Io and Eo the current and voltage amplitudes, respectively.

The EIS spectrum gives impedance (which includes real resistance, imaginary resistance, i.e. the system capacitance) and phase shift vs. frequency of the incoming signal. The frequency is normally changed between 10 kHz and 0.01 Hz, which gives possibility to investigate electrochemical processes of different rates.

Immersion of metal in water solution creates double electric layer – metal/electrolyte, which properties have response at the low frequencies. In this range the spectrum of a metal surface includes information on values of the surface capacitance and the resistance of the metal to corrosion. In the middle frequency range the influence of performed corrosion products, e.g. passive oxide films, could be observed. At the high frequencies the response from dielectric porous films like polymeric and inorganic coatings can be found. From the real resistance, given at the high frequency, the solution ionic conductivity can be evaluated. By using EIS important information can be received for corrosion rate (e.g. polarization resistance to corrosion process) and condition of the metal surface (e.g. level of passivity and presence of corrosion products).

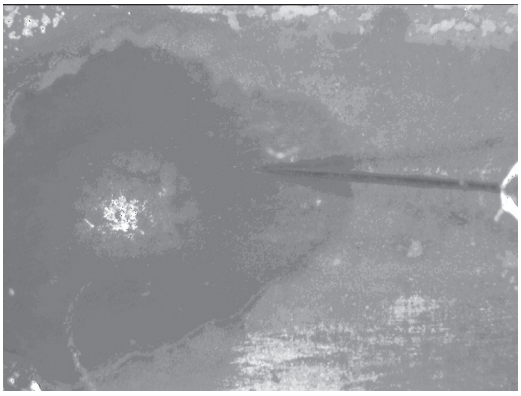


Figure 6.20: Photograph of the centre of one sample inside the SVET showing the scanning electrode.

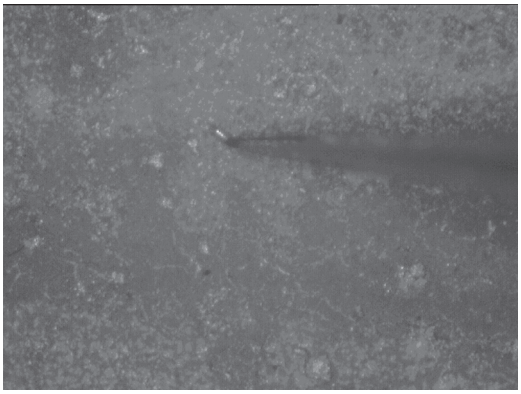


Figure 6.21: Photograph of one sample inside the SVET showing the tip of the scanning vibrating electrode after contact with the sample surface. One can see that the tip of the electrode is bent due to the contact with the surface and that it lost the platinum black deposit on its tip.

In this project samples of carbon steel, stainless steel (AISI 316L) and copper have in an exposure container been exposed to ten heat distributing systems with different water quality. For two of these, the Danish distribution and the transmission system, the mentioned samples have been analysed by EIS. The main purpose of this investigation was to see whether the EIS can be used for estimation the influence of biofilm on corrosion.

Eksperimental

The metal samples were removed from each of the two exposure units connected to the distribution and the transmission plant of Denmark (Aarhus). The samples were placed in an air tight tube, filled with system water from the respective plant, purged with nitrogen and sent to Stockholm and the Swedish Corrosion Institute (SCI) where the analyses were made. After receiving and opening the sample tubes, the samples were measured as quickly as possible. The sample was placed in an electrochemical cell opened to air, together with the belonging system water.

The EIS spectra were measured in a three-electrode system (working, counter and reference electrodes) at the open circuit potential. Between the working electrode (stainless steel, carbon steel or copper, each with a surface area of approx. 8 cm2) and the counter platinum electrode, a sinusoidal current with amplitude 20 mV was applied in the frequencies range 1 kHz-0.01 Hz. The EIS spectra were recorded using a potentiostate (EG&G 283 PAR) and a Frequency Response Analyser (FRA Solartron 1255). Open circuit potential (corrosion poten-

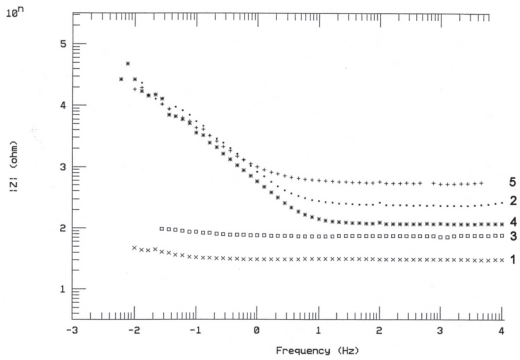


Figure 6.22 EIS spectrum for stainless steel, having the impedance as a function of frequency. Plot 1, 3 and 4 are for the distribution line, and for 1, 2, and 24 hours of exposure time, respectively. Plot 2 and 5 are for the transmission line, and for 1 and 24 hours of exposure time, respectively.

tial) was monitored by a voltammeter (EG&G 283 PAR) with software (382 SoftCorr III).

The experimental electrochemical techniques applied to biofilms at metal surfaces and the following data analyses is given elsewhere [Xu et al., 1998; Dexter et al., 1991; Mansfeld and Little, 1991].

Results

Two EIS spectra for the stainless steel surfaces are given in figure 6.22 and 6.23, giving the dependence of impedance module and phase shift on frequency respectively, both as s. c. Bode plots. For figure 6.22 it can bee seen that when increasing the exposure time the impedance value at the low frequencies increases for distribution line while is about the same for the

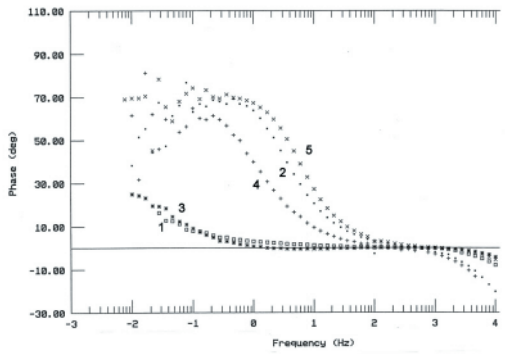


Figure 6.23 EIS spectrum for stainless steel, having the phase shift as a function of frequency. Plot 1, 3 and 4 are for the distribution line, and for 1, 2, and 24 hours of exposure time, respectively. Plot 2 and 5 are for the transmission line, and for 1 and 24 hours of exposure time, respectively.

transmission line without (curves 1,3,4 and 2,5, respectively). At the beginning (after 1 and 2 hours of exposure), the impedance of the steel from the distribution line (curve 1 and 3) is very low. This shows that the steel is present in its active state. Over the same time the steel from the transmission part is passive. It means that the protective passive film is not stable for the sample from the distribution plant, while it is for the sample from the transmission part. During exposure in distribution system water for 24 hours the impedance is increased (curve 4), and is at low frequencies close to the impedance value of the steel from the system water of the transmission line.

The experiment shows that during the experimental exposure, i.e. exposure to air, oxygen passivates the steel surface. For phase shift dependence on frequency, shown as Bode plots (figure 6.23), the different degree of passivity is clearly visible. For these plots active surfaces have low phase shift and high phase shift observed for passive samples. From figure 6.23 it can be seen that at low frequency the distribution sample has a low phase shift (20 degrees) and the transmission sample a high phase shift (70 degrees).

The impedance values at the high frequencies correspond to resistance of electrolyte (i.e. the type of tap water) and surface films attached to metal surface. It is possible to observe that impedance is lower for distribution line then for transmission line. It can correspond to a higher conductivity of the electrolyte or lower resistance of a surface film (e.g. the biofilm) for the distribution line compared to the transmission line. According to table 6.2, the conductivity for the distribution line is much higher, 130-200 µS/cm, compared to the conductivity for the transmission line, 6.3-10 µS/cm. This gives that the higher conductivity for the distribution line is at least a contributing explanation.

Spectra for all the other samples were also taken, and from which the most important characteristics are presented in table 6.2.

From the table it is possible to conclude that corrosion conditions in tap water in distribution line are more aggressive compare to transmission line for at least four reasons

- The polarisation resistance (R1) is higher and therefore the corrosion rate lower in transmission line for stainless steel and copper. The similar values were observed for carbon steel.
- R2 is a measure of the resistivity of the electrolyte, i.e. the system water. The higher value the lover concentration of ionic species. For the distribution line R2 is lower for all measurements.
- The higher the capacitance the more developed is the surface, i.e. the more have the surface reacted. For the distribution line, the capacitance is higher for most of the measurements.

- Corrosion potential is more negative and the surface is more active for the distribution line.
- Access of the oxygen in the air leads to passivation of the metals.

It is possible to compare EIS data for carbon steel in system water with data for the steel in mild aggressive 0.1M NaCl electrolyte [Itagaki et al., 2004]. In aerated sodium chloride the polarization resistance of the steel is near in 3-5 times (R1 = 250 ohm) higher comparing to our data for the system water (R1 =30 - 80 ohm). This can be an indication of that aggressive behavior of biofilms can be formed in relatively non-aggressive system water.

Biofilms supports concentration gradient parallel or perpendicular to metal surface. The films at the steels can attract the aggressive ions from the electrolyte to maintain charge neutrality in the biofilm [Mansfeld and Little, 1991]. It is possible to propose increased local concentration of aggressive ions close to the metal surface.

Table 6.2 EIS parameters. R1 is the polarization resistance, R2 the solution and film resistance, time is time of exposure in the open air cell, C is the capacitance and E is the corrosion potential.

Plant	Alloy	Time	R1	R2	C	E
		hours	ohm	mF	mV	
Distribution line	Stainless steel	1	12	76	312	-615
		2	13	79	337	-515
		24	10 300	116	0.458	-50
	carbon steel	1	30	45	168	-387
		2	56	43	67	-670
		24	87	61	89	-250
	copper	1	705	45	7.6	-125
		24	730	35	5.9	-14
Transmission line	Stainless steel	1	6540	213	0.403	-14
		2	14260	222	0.32	-92
		24	15100	245	0.24	-15
	carbon steel	1	118	183	73	-673
		2	22	307	97	-610
		24	75	470	82	-655
	copper	1	2610	540	1.8	28
		2	1540	520	3.2	36

7 Evaluation of parameters for assessing risk of mic

The involved plant personnel was asked to provide informations regarding: basic data for the plant, plant history, and water quality during the survey. Apart from a single plant, information has been received from all plants involved. The information on water quality obviously depends on the extent of the monitoring program carried out at each plant. Thus, a comparison on all parameters is not possible. Table 7.1 shows the available data for the ten sites. Ranges indicate that several measurements have been conducted during the survey yielding data within the given range.

Conclusions from the previous section regarding MIC versus non-MIC are indicated in the table too.

Of the two plants where the corrosion has been concluded to be MIC with a high degree of certainty, data is unfortunately only available for one. Nonetheless, concentrating on this one, there are three parameters that stand out.

The pH at the Southampton plant is quite low at 8.8 compared to the other plants. Persons affiliated with the Southampton plant agree that recently it has been difficult to maintain a high pH in the system; particularly in some local areas.

The water in Southampton also shows the highest concentration of chloride. This fact is, however not thought to influence the microbiological activity within the water, but may certainly influence corrosion.

Table 7.1 Plant data including analysis of system water during the survey period. Shades: dark gray: MIC, light gray: possibly MIC/initiating MIC, white: non-MIC.Heavy frames indicate possible links to water quality

Site / Parameter	Unit	Budapest	Děčín	Helsinki	Lemgo	Lienz	Southampton	Stockholm - Hässelby	Stockholm -Värtan	Aarhus - Distribution	Aarhus - Transmission
Build	Year	1960	2002	1957	No data available	2003	1990	1951	1961		
Original feed water								Softened	Softened		
Present feed water		De-ionised	Partly de-ionised			Partly de-ionised		De-ionised	De-ionised	Partly de-ionised	De-ionised
Temperature	°C		55-90(110)	35-120			50-85	35-120	35-120		
pH		9	9,5	9,6		9,6	8,8	9,5-9,9	9,3-9,9	10,2-10,4	9,4-9,5
Conductivity	µS/cm	25	300	125		130		14-18	41-52	150-200	6,3-10
Hardness	°dH	0,1		0,06		0,02	12ppm CaCO3			0,3-0,6	<0,3
O_2	µg/l			<5							
Cl	mg/l	4		5			40			6-9	<0,5
F	mg/l							0,02-0,1	0,08-0,35		
Ca	mg/l							0,08-0,26	0,18-0,98		
PO_4	mg/l					0,69				0,1-0,3	<0,1
Fe	mg/l			0,05		0,09	<0,5			0,3-0,6	<0,05
NH_3	mg/l									0,7-1	0,9
Sulfite	mg/l	1	5				45				
N_2H_4	µg/l			200							
Pyranin	mg/l			0,5							
P_2O_5	mg/l		10								
p	mmol/l	0,04	0,5			0,16				0,6-0,9	0,03-0,08
b	mmol/l									0,6-0,8	0,05-0,12
m	mmol/l	0,35				1,12					
T	mmol/l		0,005								

Southampton is also among the plants that use sulphite as oxygen scavenger, keeping the highest residual concentration within the survey: 45ppm. Sulphite may in terms be utilised by the sulphate reducing bacteria in their production of sulphide. The facts that pointed towards MIC at Southampton were a large number of bacteria, and presence of both sulphide rich minerals and SRB. The sulphite along with organic matter and other nutrients is believed to play an important role in the overall MIC process.

The two other plants to analyse for sulphide: Budapest and Děčín are within the group of possible MIC/initiating MIC.

Helsinki, belonging to the group non-MIC, showed a very low concentrations of cells and no SRB. Looking at the water quality reported from Helsinki, this may have something to do with addition of the somewhat toxic hydrazine as oxygen scavenger. Sulphide rich minerals were identified in Helsinki, but they are thought to originate from local areas within the system where the hydrazine may be depleted (e.g. within sludge in storage tanks).

Another parameter that seems to affect the corrosion for three plants, is the presence of a pH buffer. The plant in Lienz uses phosphate to adjust pH while the two sites in Aarhus use ammonium. The fact that the water contains chemical substances that buffer the pH, is thought to minimise the effect of biofilm. The effect of all acidifying processes within the biofilm will be limited by the presence of a sufficient amount of buffer and the resulting local pH at the surface will thus be higher.

8 Conclusion

Performing this survey had two basic purposes: 1) to find out if the biologically related corrosion problems currently experienced in Danish DH systems may be threatening the integrity of other DH plants and 2) to try to establish a connection between identification of microbiologically influenced corrosion and the system parameters generally available in order to assess the risk of MIC in DH plants in general.

As a secondary objective, methods used today to assess corrosion and fouling in DH systems were evaluated, and a number of new and potentially useful methods were tested.

Biocorrosion survey
Biofouling, corrosion and their combined effect, microbiologically influenced corrosion, were evaluated within ten DH plants:

- Budapest, Hungary
- Lienz, Austria
- Lemgo, Germany
- Southampton, United Kingdom
- Helsinki, Finland
- Děčín, Czech Republic
- Stockholm, Sweden (two plants: Hässelby and Värtan)
- Aarhus, Denmark (two plants: Transmission and Distribution)

Two coupon exposure methods were used associated with two sets of basic analytical techniques. The outcome was evaluated in terms of stating MIC or non-MIC for each plant.

The corrosion within two out of the ten plants (Southampton and Lemgo) was categorised as MIC.

Four plants (Budapest, Děčín and the two plants in Stockholm) experienced corrosion that was categorised as either ”possibly MIC” or ”initiating MIC”. The category ”possibly MIC” means that there were clearly other factors influencing the corrosion though all prerequisites for MIC were present. ”Initiating MIC” means that weak indications for MIC were observed, which could possibly explain the corrosion.

In the remaining four plants (Lienz, Helsinki, and the two sites in Aarhus) either no corrosion was observed or the corrosion was clearly not influenced by microbiological activity.

Evaluation of basic analytical techniques
Of the two methods for exposing corrosion and fouling coupons, one simulated pipe flow, the other stagnant conditions. The construction materials used for the stagnant water unit allowed for small amounts of oxygen to reach the coupons, the other was made of stainless steel. Looking at the data from the two units, the one simulating pipe flow gave the largest variations among the plants, while the results from the other showed only minor variations.

Some of this may be due to the different analytical methods used to investigate coupons from the two units.

The corrosion methods using weight loss could not be questioned, but the evaluation of localised corrosion was only possible on coupons from the pipe flow unit. Out of the two methods used to evaluate the total number of bacteria, only the one utilising DAPI staining of bacteria transferred to sterile filters proved to have the necessary width to cover both the low and the high end of the biofouling scale.

A number of growth-based methods were used to evaluate the biological community. However, these methods were only able to cover a maximum of 0.1% of the total number of cells. Thus the bacteria taking action in the MIC processes may not be found using these methods.

A qualitatively growth-based analysis of the ability of the bacteria to reduce sulphate to sulphide, which has been used extensively and with good results in Denmark, proved to be inadequate when applied to most DH plants. On the contrary, a simple spot test for testing the presence of sulphide rich minerals turned out to be a powerful tool to detect the present or previous actions of SRB.

Test of new techniques
The methods tested covered two levels of x-ray fluorescence, a molecular biology technique called FISH, and a number of localised electrochemical techniques.

Using X-ray fluorescence in a bulk mode allowed for in-situ quantification of the elements present within deposits directly on the coupon surface. Using a mapping mode of the same technique, it was possible to obtain images of the spacial distribution of the elements. For example the sulphide in Southampton deposits was solely associated with corrosion attacks, whereas the sulphide in Hässelby deposits was more spread out.

The FISH technique allows for in-situ determination of various bacterial groups without growing the bacteria in artificial media. The cells are stained directly according to their placement in the phylogenetic tree. The method did, however, not prove to be useful for in-situ purposes. Thus, it was not possible to obtain information on the spatial correlation of bacterial groups and corrosion attacks. FISH could instead be used on samples scraped off the corrosion coupons, homogenised and mounted on sterile filters. In this case the best results were obtained with samples not containing substantial amounts of corrosion products.

The localised electrochemical methods, which had been suggested as particularly useful in terms of illustrating the local corrosion processes, were unfortunately not successful. It turned out that even the small curvature of the samples from the pipe flow unit interfered so much with the measurements that these did not give meaningfull results. The potential of the methods was though illustrated and one of the methods was demonstrated in a macroscopic mode in case the problem with the curvature is solved.

MIC risk assessment
Comparing the observations of MIC and non-MIC with plant parameters obtained during the survey, gave some indications of what could lead to MIC and what should not.

Particularly the use of chemical additives seemed to play a major role in MIC. The following was observed as indications:

- Addition of sulphite as oxygen scavenger increases the risk of MIC
- Addition of hydrazine lowers the risk of MIC but other corrosion problems may occur
- Keeping a relatively low temperature results in higher risk of MIC
- Not maintaining a sufficiently high pH increases the risk of MIC
- Addition of phosphate buffers the pH and lowers the risk of MIC
- Addition of ammonium has similar effects and lowers the risk of MIC

These indications are, of course, limited by the situation at the plants participating in the survey. The statements may be verified and expanded by expanding the survey to other plants

Recommendations
Based on our experiences during the survey we have accepted that MIC is not only a Danish problem, but potentially a problem to all DH installations. We thus recommend that microorganisms and the problems they obviously create in many plants are taken seriously, as they could otherwise significantly limit the lifetime of the installations.

On identification and monitoring of MIC we recommend that corrosion coupons are used either directly within the system or within a side stream exposure unit like the pipe flow unit used in this study.

For corrosion measurements we recommend that measurements of general corrosion rates are accompanied by topographical analysis of local corrosion since the local rates are often much higher than the general ones.

Growth-based methods for monitoring biofouling are time consuming and have not proven to be useful in this survey. It is thus recommended to use total counts (by staining) for determining the level of biofouling. Identification of SRB, which often play an important role in MIC, is difficult to obtain in DH systems. Their by-product, sulphide, may though be identified through a simple spot test for sulphide rich minerals.

Finally, it is recommended to use X-ray fluorescence in the case detailed investigations of possible MIC attacks are needed. The method has proven to be applicable without any further developments.

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