



Monitoring corrosion in district heating systems

Project number: 00071

Final Report

May 2004

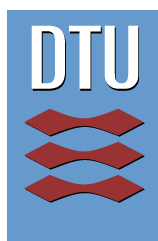
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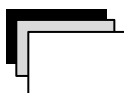
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STAVANGER
UNIVERSITY
COLLEGE



Korrosionsinstitutet
Swedish Corrosion Institute

Summary

The project started in April 2001, formally with a kick-off meeting on May 28 2001 at the FORCE Technology in Denmark. The main focus was on the application of known, as well as new corrosion monitoring techniques in district heating systems, and to evaluate whether the information obtained was reliable and thus, of use to the district heating plants. One aspect was how the water chemistry and choice of technique as well as interpretation of data were related. This was connected to the mechanistic studies of how water chemistry affects corrosion rates and forms of corrosion. Laboratory as well as field studies were necessary to clarify these aspects. General corrosion is known to occur very slowly in district heating water systems, however, the aspect of crevice corrosion is of more interest. This form of corrosion is more critical than general corrosion, and more difficult to monitor and quantify. Also microbial induced corrosion (MIC) has been difficult to monitor and has so far been based on periodically withdrawal of coupons.

The results obtained relate to probe design, modification of instrumentation and laboratory studies of electrochemical and electrical resistance (ER) measurements with temperature compensation in solutions with low conductivity (20 $\mu\text{S}/\text{cm}$) and in sulphide containing deaerated water. Test rigs for in-situ measurements, which give the possibility to measure general corrosion, pitting corrosion, crevice corrosion and microbial corrosion, have been designed and tested. The measurement methods in-situ were the direct methods; weight loss (WL), high sensitive electrical resistance (ER), and the crevice corrosion cell and the electrochemical methods; electrochemical impedance spectroscopy (EIS), linear polarisation resistance (LPR), zero resistance ammetry (ZRA) and electrochemical noise (EN), together with monitoring of pH, conductivity, dissolved oxygen, sulphur compounds and bacteria. The measurement data has been automatically transferred by GSM SMS data transfer. Experiments on sulphur compounds by cyclic voltammetric (CV) analyses have been performed. Moreover, different qualities of district heating and cooling water have been studied with respect to their ability to favour presence and growth of micro-organisms.

The project gained positive synergies through the collaboration as the participants covered different aspects of the corrosion process in district heating systems. The collaboration strengthened the solidarity between the partners and increased the knowledge in the area. Several meetings were held in the respective subprojects, and furthermore, the respective subproject managers were in contact discussing solutions and writing articles. The project has been presented widely, e.g. at the 15th International Corrosion Congress in Granada 2002, at Eurocorr in Budapest 2003 and the 13th Scandinavian Corrosion Congress in Reykjavik 2004.

Eight engineering students have been active in the project. A Ph.D. student from Iceland visited DTU in Denmark for six weeks in November-December 2001 and for four weeks in June 2002 to study corrosion monitoring techniques. In August 2002 she visited Stavanger University College and in May 2003 Helsinki University of Technology. In addition three Danish chemical engineer students have finished their bachelor project on corrosion monitoring. Two students from DTU were trainees at FORCE Technology during autumn 2002 and one trainee from DTU worked at IBRI from September 2002 until January 2003. Furthermore, a Ph.D. student from Stavanger University College visited IBRI in March 2004.

The project has resulted in development of new methods and directions for choice of reliable methods for online monitoring of corrosion rates in district heating and cooling systems. It is

recommended to use two methods simultaneously for continuous corrosion control in these systems. In Finland it is recommended to use ZRA and LPR, LPR measures the corrosion rate and ZRA is able to detect minor changes, e.g. an increase in oxygen concentrations due to water additions. In Denmark it is recommended to use high sensitive ER-technique developed by MetriCorr and the LOCOR-cell developed by FORCE technology for future district heating corrosion monitoring. In the geothermal systems in Iceland ZRA and LPR or ER is applicable. For ZRA measurements the LOCOR-cell could be used or even simpler a copper/iron probe. Both methods are sensitive to sudden changes in the water chemistry and can alarm if e.g. the oxygen level goes up. LPR and ER resulted in reliable corrosion rates, but care has to be taken in case of LPR measurements in choice of polarisation rates and the algorithm to calculate the polarisation resistance. The LPR method was not successful in the Danish systems.

EIS can measure the polarisation resistance, but the test takes long time (several days) and the evaluation of the results is complicated and prone to failures. Hence, EIS is not recommended for online monitoring.

The SmartCET[®] system from Intercorr in USA was tested in Denmark and Iceland. The system is based on EN, LPR and HDA¹ measurements. The LPR measurements resulted in too high corrosion rates, probably due to the high scan rates in the system, which could not be adjusted. The EN-measurements could detect sudden changes in the system and could prove successful together with adjusted LPR measurements or the ER technique.

Online oxygen measurements with instruments from Oxyguard in Denmark were successful in the Danish district heating systems. However, in the geothermal system in Iceland the equipment was only stable for 7-10 days and then the values got too low. The presence of sulphide in the geothermal water makes it difficult to develop online equipment for oxygen monitoring.

Combining the CV and/or optical measurements by camera to other techniques may be useful in studying the reactions of e.g. sulphur compounds in district heating water and for monitoring film formation.

Detection of microbial corrosion by online methods is hardly possible and the use of coupons is preferred. Biofilm is formed on all exposed coupons and it will always be difficult to relate corrosion problems directly to micro-organisms. However, the developed online methods will measure the corrosion rate and follow changes in the system, regardless of the corrosion causes.

¹ Harmonic distortion analyses enables a direct measurement of the Tafel slopes and the Stern-Geary constant (also referred to as B-value).

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I Background of the project

The Nordic countries are known for their skills in building and operating district heating networks, which are increasingly applied in the world and known as economic and environmentally sound solutions. Corrosion in district heating systems in these countries is normally at minimum, due to negligible oxygen content, low conductivity and appropriate pH values. Though, corrosion is occasionally responsible for leaks or scaling problems in some systems.

Uniform corrosion is known to occur slowly in district heating water systems however the aspect of local corrosion attacks is of more interest. This form of corrosion is more critical than general corrosion and more difficult to monitor and quantify.

It is well known that oxygen is the main factor regarding corrosion attacks, but in recent years other parameters have been investigated, and corrosion measuring techniques developed. Effort has been made to estimate the corrosion effect of oxygen ingress, sulphur compounds, pH-values and micro-organisms.

District heating companies have to choose between various water treatment methods and operating parameters. The cost can vary widely and it can be difficult to decide the optimal choices. It is uncertain which type of oxygen scavenging should be used. Other uncertainties involve ingress of oxygen, e.g. in heat accumulators and in which extent this can be avoided, the effect of intermediary sulphur compounds e.g. sulphite and thiosulphate, which have been found responsible for crevice corrosion and pitting, the presence of micro-organisms in the system and their possible growth by adding corrosion inhibitors, and the effect on corrosion. Furthermore, it is questioned if it is possible to control pH within the narrow boundaries as recommended.

The techniques tested are various electrochemical measurements, electrical resistance, microbial methods and weight loss coupons. The weight loss coupons have given good results on the average corrosion rate. However, this method is time consuming and therefore other methods are tested to follow the momentary corrosion rate and to discover possible crevice corrosion or microbial corrosion. The main problem so far has been the reliability of the measurements. Also it has not proven successful to measure microbial corrosion on-line.

The objective of the project was to design methods for in-situ corrosion measurements that give the possibility to monitor uniform corrosion, crevice corrosion and microbial corrosion and relate the results to water parameters. It is important that future methods for monitoring are simple, give clear results, are valid, and well documented. Furthermore, the measurements should quickly show unfavourable changes in the system. Therefore, on-line monitoring, possibly with automatically transfer of data by GSM SMS was aimed for.

II Water treatment in district heating systems

District heating water normally has a low conductivity, low oxygen content and high pH. Therefore, the corrosion rate is most often minimal. However, critical corrosion attacks may occur in form of localized attacks. The attacks can happen due to ingress of oxygen, localized pH differences or sulphur compounds. Furthermore, these factors interact, e.g. the sulphur chemistry varies with oxygen content and pH.

In aqueous heating systems, the water is circulated, and it is possible to control the environment to avoid corrosion. Therefore steel is a commonly used material in district heating systems, the production cost is low and construction qualities are good.

In order to obtain the non-corrosive environments, the water is treated in several ways. The various water treatments are conducted to obtain one or more of the following qualities: Suitable pH-level, low hardness, low oxygen content, low conductivity, low level of chlorides and sulphur compounds and low level of solid particles. Additionally, corrosion inhibitors and oxygen scavengers can be used.

Fresh water is the usual source for process water for the plants and the varieties of the pre-treatments of the water are numerous.

Water treatment in Denmark

Many levels of treatments are used in practice. The process water can be classified as untreated, softened, partly desalinated or desalinated. As an example of specifications for each of these different types of process water are given in table 2.1.1. The table contain some of the specified criteria from code of practice described in DFF (Danish District Heating Association).

To maintain these systems the additional water for the plant can either be unconditioned, pH-adjusted and/or oxygen can be reduced by deaeration or by addition of an oxygen scavenger. If oxygen is not removed from additional water before use at the plant and no oxygen scavenger is used, then the oxygen content in the process water will be quickly removed by corrosion of the steel constructions.

Thus the different plants make their choice for water treatment. The methods for deaeration can be either vacuum- or steam-deaeration. In some cases micro bobble deaeration is used as partly deaeration. As oxygen scavengers a number of chemicals can be used. Before, hydrazine was widely used, but it is not used today for environmental reasons. Sulphite is seldom used as earlier experiences have shown that sulphur compounds can introduce increased corrosion of copper and copper phosphor brazing metals. In many cases tannins are used, but it results in addition of huge amounts of organic substances to the water, which can increase growth of micro-organisms.

Table 2.1.1. Process water. Extract of water parameters from the DFF (Danish District Heating Association) quality classes for process water in district heating systems.

Quality class	Untreated	Softened	Partly desalted	Desalted
Additional water	Drinking water	Softened water	Softened and/or desalted	Desalted water
Solid particles ppm	< 10	< 10	< 5	< 1
Oil and grease content ppm	< 1	< 1	< 1	< 1
pH at 25°C		9.8 ± 0.2	9.8 ± 0.2	9,8 ± 0.2
Rest hardness of the water °dH		<0.5	<0.2	<0.1
Conductivity at 25°C µS/cm		< 1,500	< 500	< 25
Oxygen ppm		< 0.02	< 0.02	< 0.02
Chlorides ppm	< 300	< 300	< 50	< 3
Sulphates ppm				< 2
Ammonia ppm		< 0.02	< 0.02	< 0.01

Other ways of treating the circulating water can be to use the same inhibitor systems, which are used for cooling systems. This is mixtures of anodic and cathodic inhibitors, chosen to protect all the relevant metals.

Water treatment in Finland

The tap water of city Mikkeli is pumped through a softener. As a oxygen scavenger Advantage-K-550 (Ashland) is utilized according to analyses (0,1 - 1,0 ml/m³ surplus). Advantage-K-550 increases also the pH value of the water.

Water treatment in Iceland

The district heating systems in Iceland mainly use geothermal energy. The distribution systems are most often once-through and the hot water is used both for heating purposes and as hot tap water. The geothermal fields are by definition divided into high temperature and low temperature areas. In the former the temperature is above 200°C at 1.000 metre depth, whereas in the latter the temperature is below 150°C at the depth of 1.000 metre.

Most district heating systems in Iceland use low temperature geothermal water, which is normally distributed directly from the boreholes to the consumers. Water from the high temperature geothermal fields is not suited for direct use, due to high risk of scaling and corrosion of pipelines. The mineral content is high and the steam contains some non-condensing gases, mainly carbon dioxide and hydrogen sulphide. In those systems cold ground water is heated by geothermal steam and hot water in heat exchangers. The water is deaerated by vacuum boiling in order to remove the dissolved oxygen and in some systems a small dose of geothermal steam containing H_2S is injected to the water to react with oxygen that may enter the distribution system and to lower the pH of the water and thereby lower the supersaturation with respect to magnesium silicates. The heated fresh water is then distributed and treated in the same way as the low-temperature water.

Water treatment in Norway

District heating systems do not follow any particular procedure recommendations. Often external consultants are involved in setting up the chemical parameters for the systems. The recommendations from the Nordvarme report² are often used as basis. In systems in Hamar and at Gardermoen, built for approximately 50 GWh/year, the circulating water passes a rough filter, and part of the stream is run through a fine filter in order to remove magnetite and smaller particles³. For added water, ion exchange filters are used to reduce the hardness of the water and degassing is used for oxygen removal. Sodium hydroxide is added in order to achieve a pH in the range 9 to 10.5. The addition of chemicals is avoided whenever possible.

The Elysator system is based on magnesium electrodes, which react with oxygen and form magnesium hydroxide. This system is used in approximately 500 heating systems in the Nordic countries⁴. The manufacturer of the system claims that a lower magnetite concentration and reduced sludge production is observed, and that a relatively low conductivity is achieved.

E-CO Partner has given the following recommendations under start up at Klemetsrud Kraftvarmeverk⁵.

Table 2.4.1. Recommendation under start-up at Klemetsrud Kraftvarmeverk in Norway.

	Recommended values in Nordvarme Report, RE-3/1990	Recommended values from Hans Wistrand, AB
pH	9,5-10,0	9,0-10,5
O ₂ , mg/kg	<0,02	<0,02
Conductivity, µS/cm	<50	
SiO ₂ , mg/kg	See new instructions	See new instructions
Fe, mg/kg	<0,10	<0,10
Cu, mg/kg	<0,02	<0,02
KMnO ₄ , mg/kg	<10,0	<10,0
Hardness, °dH		<0,10

Water treatment in Sweden

The guiding principles for the water treatment and water quality are to some degree depending on the type of heat distributing system. The heat distributing system can be divided into three groups. The heat carrier of the heat producer is either steam or water, and if water is the heat carrier, either the same water circulates through the heat producer and the district net (direct system) or it is separated by a heat exchanger (indirect system). No reliable statistics are available regarding the share of the total heat delivery of the heat distributing nets between the three different types of heat

² Nordvärme, Korrosion och vattenbehandling i nordiske fjärrvarmesystem (1990).

³ Mats Rosenberg, Enercon AS, private communication.

⁴ Tor Halvorsen, Arcon AS, private communication.

⁵ John Bongard, E-CO partner, private communication.

distributing system, but a fairly reliable, although rather rough estimation is that the heat production is equally divided among them.

The guiding principles for the water treatment can be seen in table 2.5.1, for the water quality of the district heating net in table 2.5.2 and for the making up water in table 2.5.3. The presented guiding principles have been formulated by the district heating association of Sweden.

Table 2.5.1. Swedish guiding principles for the treatment of water for district heating net.

	Direct system; Power plant	Direct system; Heating boiler	Indirect system; Heating boiler
Supplement water	Totally de-ionised	Softened	Softened & de-ionised (if >50ppm) & decarbonated (if >60ppm)
Degasification	Thermal	Thermal or chemical	Thermal
Water cleaning	Sludge hopper & mechanic filter & de-ionisation	Sludge hopper & mechanic filter & water softener	Sludge hopper & mechanic filter & water softener
Additives	NaOH and oxygen binders	NaOH and (oxygen binders or inhibitors)	NaOH and (oxygen binders or inhibitors)
Analyses	pH, hardness, additives, iron, copper		

Table 2.5.2. Swedish guiding principles for the quality of the water for district heating net.

		Indirect system	Direct system	
Analyte	Unit		>10MW	<10MW
pH (25 °C)		9.5-10	9.5-10	9.5-10
Hardness	mmol/kg (°dH)	<0.178 (<1.0)	<0.018 (<0.1)	<0.089 (<0.5)
Oxygen	mg/kg	<0.02	<0.02	
Ammonia	mg/kg	<10	<10	
Iron	mg/kg	<0.1	<0.1	
Copper	mg/kg	<0.02	<0.02	
Oil, fat	mg/kg	<1	<1	

For the water quality of the district heating net values, recommendations for the conductivity do not exist, but generally it is regarded that the lower the conductivity the lower the corrosion rate.

Table 2.5.3. Swedish guiding principles for the quality of the making up water to district heating net.

Analyte	Unit	Degassed and softened	Degassed and deionised
Conductivity (25 °C)	mS/m	as in raw water	<1.0
Hardness	°dH	<0.1	<0.01
Hydrogen carbonate	mg/kg	<60	
Oxygen	mg/kg	<0.02	<0.02
Carbon dioxide	mg/kg		<10

III Corrosion measurement techniques

The corrosion measurement techniques used are weight loss coupons, various electrochemical methods, electrical resistance and microbial corrosion measurements. Furthermore, the sulphur chemistry is studied by cyclic voltammetry and galvanic measurements.

Weight loss coupons

The use of weight loss coupons is simple methods, which is based on weighing the samples before and after immersion in the medium and calculating the corrosion rate, see e.g. ISO 11845⁶ and ISO 8407⁷.

The weight loss coupons have proven successful in the systems to measure the average uniform corrosion rate. However, this is a time consuming method and it does not detect sudden changes in the water chemistry nor local corrosion attacks.

Electrochemical techniques

Monitoring techniques that provide on-line, real time detection of corrosion rates and possible changes are available. Electrochemical data give indirect information about corrosion phenomena, which can be analysed directly. The results should also be correlated with weight loss data on a regular basis.

Linear polarisation resistance (LPR)

Linear polarisation resistance is commonly used in commercial instruments to measure uniform corrosion. LPR makes a direct measurement of current vs. potential within 10 mV of the free corrosion potential E_{corr} , assuming that in this range the current density is approximately linear with the applied potential. Stern and Geary showed that in this range, the corrosion rate is inversely proportional to polarisation resistance R_p at potentials close to E_{corr} (ASTM Standard G96-90 (96)). The resistance measurement obtained in the LPR technique represents the sum of the polarisation resistance R_p and the solution resistance R_s . A large IR drop (large R_s) caused by the low conductivity of the electrolyte, e.g. in district heating water, can result in errors in measuring R_p (Fig.3.2.1). When the electrolyte conductivity is lower than 0.5-1 mS cm⁻¹ (dependent on the probe geometry), it is necessary to measure the ohmic drop in the solution in order to calculate the correct corrosion current, as shown in Fig. 3.2.1 for a specific probe⁸.

⁶ ISO 11845 Corrosion of metals and alloys – General principles for corrosion testing

⁷ ISO 8407 Corrosion of metals and alloys – Removal of corrosion products from corrosion test specimens

⁸ Perboni G., Radaelli M., Monitoraggio elettrochimico ad alta temperatura del trattamento ossidante nel generatore di vapore con corpo cilindrico di Turbigo 4, Report ENEL-SRI-PDM-CPC-98-003, Lugio, 1998

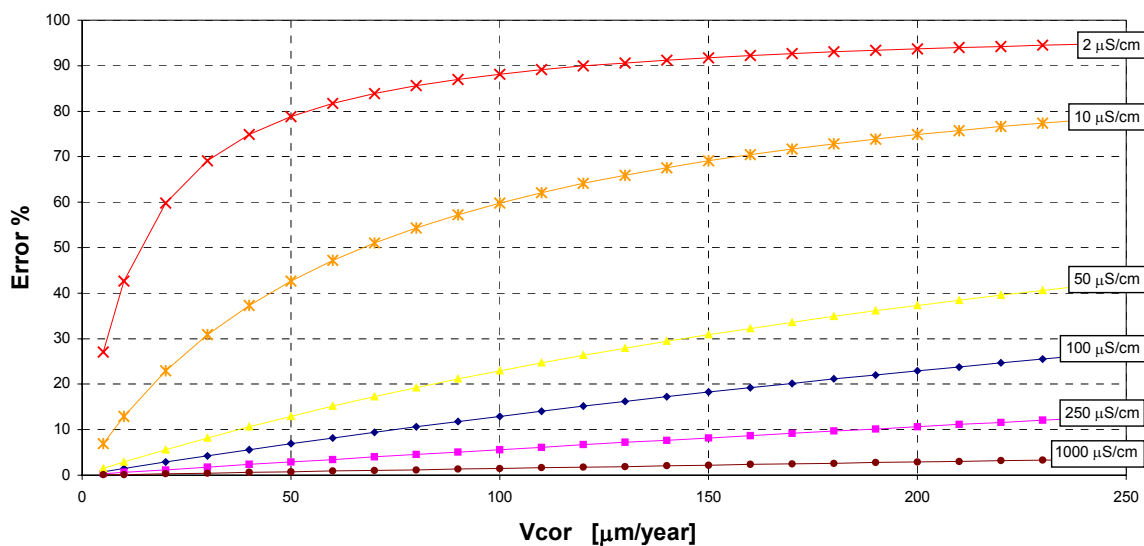


Fig. 3.2.1. Error due to ohmic drop in the determination of corrosion rate (V_{cor}) by LPR technique using a tubular probe in different solutions. For low conductivities it is recommended to measure the cell constant of each corrosion probe in order to correct V_{cor} for ohmic drop contribution.

If this parameter is the only error, low corrosion rates can be determined with rather good accuracy. However, the analysis with the LPR technique is valid if there are no other electrochemical reactions contributing to the response of the interface, which would make the interpretation very complicated. Little (1990)⁹ reported that problems could occur with use in microbially influenced corrosion (MIC) testing because the biofilm layer itself behaves as a resistance with a magnitude inversely proportional to the corrosion current, and the interface could act as a combination of parallel resistance-capacitance because of intermediate reactions. Moreover, the LPR technique overestimated corrosion in cases of a high capacitive current, when measuring corrosion on carbon steel in an anaerobic sulphate reducing bacteria (SRB) or sulphide environment¹⁰. So the technique has the following limitations: a high conductivity of the media is preferred (more than 0.5-1 mS/cm, dependent on geometry of probes) and the scan rate must be adjusted according to the time constants of the system. Care must be taken not to misinterpret data in cases of high capacitive current.

Nevertheless, because of the simplicity of measurement and instrumentation, the technique is widely used.

Open circuit potential measurement (OCP)

Measurements of the open circuit potential (OCP) of a metal probe with respect to a reference electrode is simple to use. However, for application in district heating systems problems could occur if the reference electrode is not stable in the media or with time. In very low conductivity water most reference electrodes will have difficulties stabilising.

⁹ Little B.J., Ray R.I., Wagner P.A., Jones-Meehan J., Lee C.C., Mansfeld F., (2000), Diagnosing microbiologically influenced corrosion, COST 520 Biofouling and Materials, Third International Workshop 31 May – 3 June, Budapest

¹⁰ Hilbert L.R., (2000), Monitoring microbially influenced corrosion, Ph.D.-thesis, Technical University of Denmark

OCP gives clear information on active-passive behaviour of some metal surfaces and on the modification caused by MIC, e.g., for stainless steels. OCP is also useful for carbon steel, especially if compared with the corrosion rate, but it does not directly provide corrosion information.

Electrochemical Impedance Spectroscopy (EIS)

EIS is an alternating current polarisation technique in which an e.g., sinusoidal potential perturbation is applied to the electrode over a high frequency range (e.g. from mHz to MHz) as in ASTM G106-89 (1994). The use of this sophisticated method is especially favourable for non-conducting and semi-conducting films or in media with low conductivity. EIS has been applied for MIC studies and monitoring with variable success. High capacitances can occur for steel in a sulphide environment leading to very long measurement times, in the range of hours¹¹. This technique is mainly applied in laboratory experiments and provides better information than LPR, for mechanistic studies in particular.

A general limitation of this technique is that the data interpretation is not simple and requires specialist knowledge. Nevertheless, if the system characteristics are known, the analyses could be simplified. In Fig. 3.2.2 the basic equations for the correlation between applied potential E and resulting current i is given as a function of angular frequency ω , resulting in impedance Z . Electrochemical interfaces are modelled by equivalent circuits and data presented in Nyquist or Bode plots.

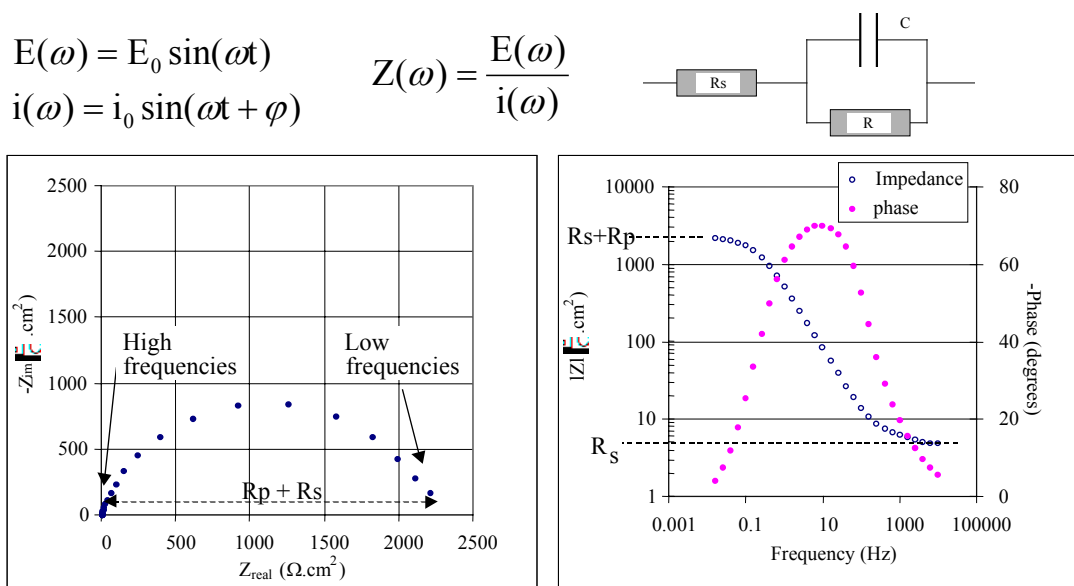


Fig. 3.2.2. Basis and response for a simple system analysed by Electrochemical Impedance (EIS) technique.

For roughly estimating corrosion rates the technique has been shown to be useful, with the same limitations for carbon steel in anaerobic sulphide media as LPR.

¹¹Hilbert L.R., (2000), Monitoring microbially influenced corrosion, Ph.D.-thesis, Technical University of Denmark

Electrochemical Noise (EN)

EN is a non-destructive measurement of potential or current fluctuations (noise) generated by electrochemical processes. EN is claimed to characterize corrosion mode, mechanism and rate, and EN is thus increasingly being commercialised for industrial monitoring.

EN is conducted on two identical electrodes at the open circuit potential without applying an external signal. This technique is able to distinguish localized corrosion from general corrosion. Good results have been obtained by combining this technique with corrosion rate measurements in laboratory applications to study the effect of SRB and other organisms on the formation of an iron sulphide film contributing to pitting corrosion of reinforcing steel and concrete¹².

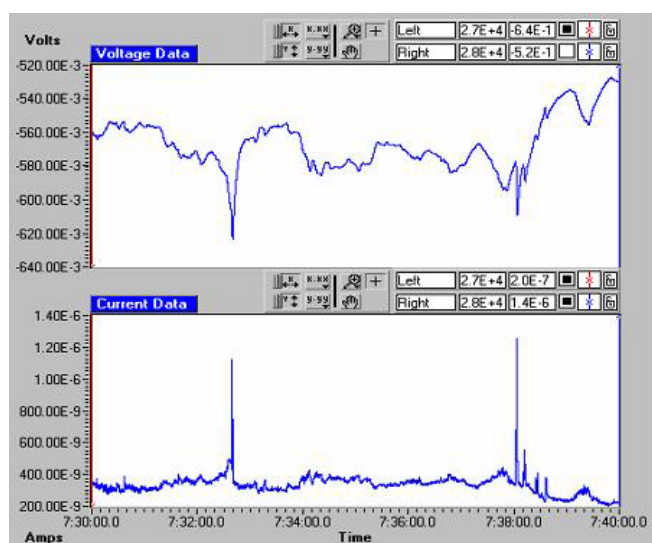


Fig. 3.2.3. Example of EN data of potential and current fluctuations.

One critical aspect of this technique is the complex analysis and interpretation of data. EN data are analysed in time and frequency domain to find e.g. the noise resistance R_n which is the ratio between the standard deviation of the potential noise σ_V and the standard deviation of current noise σ_I . The pitting index or localisation index is given by $PI = \sigma_I / I_{rms}$, where σ_I is the standard deviation of the current noise and I_{rms} is the root mean square of the coupling current.

Table 3.2.1. Interpretation of pitting index.

Pitting Index Value Range	Type of Corrosion Expected
$0.001 < PI < 0.01$	General corrosion
$0.01 < PI < 0.1$	Mixed corrosion
$0.1 < PI < 1.0$	Localized corrosion
$1.0 < PI$	Pitting initiation

¹² Little B.J., Ray R.I., Wagner P.A., Jones-Meehan J., Lee C.C., Mansfeld F., (2000), Diagnosing microbiologically influenced corrosion, COST 520 Biofouling and Materials, Third International Workshop 31 May – 3 June, Budapest

Localized corrosion probes

Zero resistance ammeter ZRA

A zero resistance ammeter can be applied especially to study localized corrosion phenomena. With this instrument it is possible to measure the galvanic current flowing freely between two separate electrodes. The ZRA is used for electrochemical noise measurements performed on standard electrodes as well as for galvanic current measurements on special designed probes like the FORCE crevice cell (see Fig. 3.3.3).

During localized corrosion as shown in Fig. 3.3.1 a current is generated between cathode and anode. If these two elements can be separated on two electrodes, the resulting current can be measured by a ZRA.

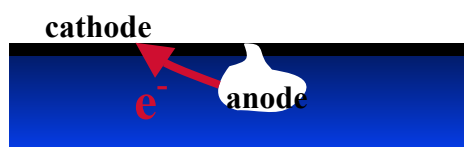


Fig. 3.3.1. Localized corrosion cell.

The separation of anode and cathode can be obtained by true galvanic probes, where dissimilar materials are coupled, or by geometrically separating the electrodes and accelerating corrosion on the anode. The latter can be obtained by electrochemical means, by creating different media and by ensuring that the size of the anode is very small as compared to the cathode.

The measured galvanic current is a quantification of the risk of localized corrosion associated with the media and geometry.

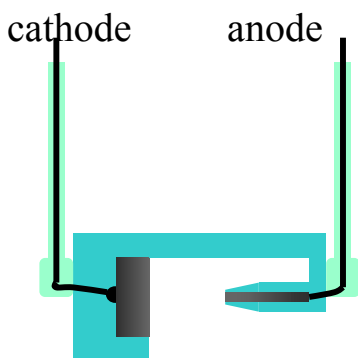


Fig. 3.3.2. Two types of localized corrosion probes applied for MIC. CABAS cell consist of concentric electrodes with the small anode in the center.

LOCOR-CELL – Monitoring crevice corrosion

The LOCOR-CELL[®] developed by FORCE TECHNOLOGY is a crevice corrosion cell based on a sensor reflecting the interaction between the environments formed under a deposit or in a crevice and the surrounding environment. It hereby simulates the corrosion conditions found on a local part of the steel surface in crevices or on areas, which is covered by corrosion products or other kinds of deposits.

The practical design implies a pure steel anode with an area of 1.77 cm² mounted in steel housing, which is threaded to fit into a normal pipe stub and is working as the cathode in the element. A glass filter plate creates the oxygen diffusion barrier on the surface, which creates the local low oxygen environment found in crevices or under deposits, Fig. 3.3.3-4.

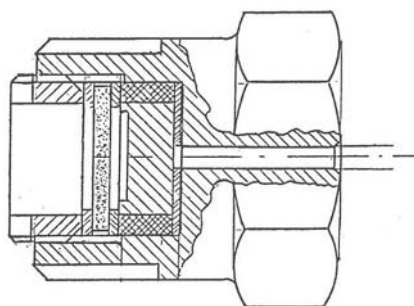


Fig. 3.3.3. Principally design of the LOCOR-Cell[®].

The covering glass filter allows ions to pass and after a period chlorides and other negative ions will accumulate in the chamber under the filter and pH will decrease. The environment at the steel anode will ensure an active corrosion site. The full area or a part of the area will easily become an anode if oxygen reaches the surrounding cathode surfaces. The size of the cathodic areas can include the cell housing and part of the actual steel pipe if the conductivity is sufficiently high.

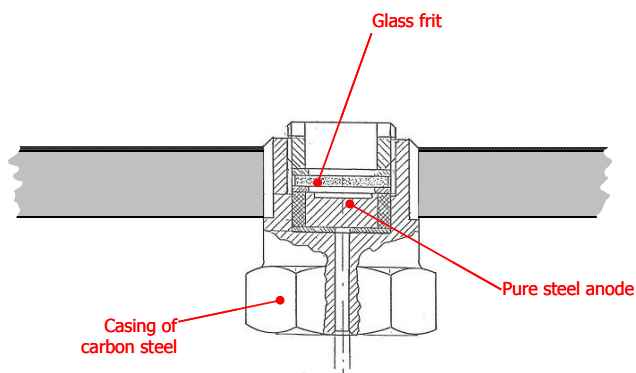


Fig. 3.3.4. Left: The LOCOR-CELL[®] shown schematically as mounted in a steel pipe. The corrosion current is measured between the steel pipe surface and the pure steel anode using a zero resistant ammeter. Right: Photo of the LOCOR-Cell[®].

The active corrosion current is measured in a zero resistance ammeter and the data can be collected in a data logger. In this project a Wenking potentiostat is used as zero resistance ammeter.

The LOCOR-Cell[®] is to be used also in inhibited cooling water and other systems where corrosion prevention is achieved by water treatment. The efficiency of the water treatment used to reduce corrosion is critical. Under deposits and in crevices this can only be measured with crevice test coupons or special corrosion cells, like the LOCOR-Cell[®].

Electrical resistance

The electrical resistance (ER) technique is a common method for measuring degree of accumulated corrosion inside a process plant.

In general, the ER-technique utilises that the electrical resistance in a metal element increases when suffering from metal loss due to corrosion. By measuring the change in electrical resistance of a metal element exposed in the corrosive environment, the degree of accumulated corrosion can be verified. Temperature changes that influence the element resistance can be eliminated by measuring the resistance in a second (similar) metal element which is shielded from the corrosive environment. The change in resistance can be attributed to metal loss.

The traditional ER technique has a rather poor measurement resolution, and consequently, the time period needed for sufficient increase in element resistance is too large measurement of the instant corrosion rate.

The purpose of the contribution by MetriCorr is to adapt a recent improvement of the technique for monitoring purposes in district heating systems. The implementation of a differential measuring technique allows for improved measurement resolution by two orders of magnitude allowing for measurement of instant rate of corrosion.

Microbial corrosion

There are no commercial instruments available that can measure corrosion on-line and directly tell whether it is microbial corrosion (MIC) or not. There is a possibility though to combine a corrosion detector with a detector for biofilms, and by comparing the results from both the devices conclude whether the occurred corrosion might be MIC. Corrosion detectors for on-line measurements are available, among them the device described in "Electrochemical techniques" and "Electrical resistance" above. However, it is more difficult to find a suitable detector for on-line measurements of biofilms. No devices for biofilm detection on-line in district heating systems was tested in this project. The most suitable devices are believed to be of the electrochemical type, from a simple home-made version using two exposed inert electrodes to the more complex and also commercial device called BioGeorge. The first device works by measuring the potential between the electrodes, which will change as biofilm is formed on one of them. The BioGeorge consists of two stainless steel electrodes where the electrodes are polarised against each other for a short period at a time. The current required to achieve the potential difference is measured, and changes when biofilms are formed on the electrodes. One advantage with this device for the owner of the district net is that it generates conditions conducive to biofilm formation, thereby giving an early signal if the water is biologically active.

Sulphur chemistry

The chemistry of sulphur is complex, both with respect to the reactions of the different sulphur compounds and the formation of different kinds of sulphide film. By use of cyclic voltammetric sweeps on a rotating ring-disc electrode the oxidation or reduction of sulphur compounds can be monitored on a platinum disc by sweeping the potential rapidly. The products formed can then be reoxidized or re-reduced on a platinum ring outside the disc at a fixed potential. By examining electrochemically different sulphur or sulphur oxide compounds over a defined pH range an overview of formed anionic products can be made.

The results from the laboratory experiments was compared with results from measurements with similar methods on site in Iceland on actual district water quality and in district water spiked with selected sulphur compounds.

If these anions react with a steel surface, a sulphide film will be formed. The film may vary with the environmental parameters such as pH, salinity, concentrations etc. By using a galvanic set-up the film formation tendency can be followed by measuring the open circuit current, while the film growth is monitored optically.

Generally, AC-impedance is a well-known method for the determination of film formation and corrosion rates. However, this method is reported to produce unreliable results when sulphide is present.

ER-measurement is a promising method, and tested in Denmark in parallel with galvanic and optic reflectance measurements in hydrogen sulphide purged electrolytes.

The optic reflectance measurements are also combined successfully with Rp-trend (LPR) and potential measurements in Norway.

Data transfer by GSM SMS

Data from LPR measurements is automatically transferred by GSM SMS data transfer. MECO2000GSM unit sends the data from Rantakylä automatically once a day to the data collection centre of Coresto Oy in city of Savonlinna. On-line measurement data can be collected also by a GSM mobile phone. The parameters of the LPR-measurement may also be changed using a mobile phone.

IV Background, activities and obtained results of the subprojects

The project is divided into six subprojects. Subproject 1 is concerned with sulphur compounds and their effect on corrosion. Subproject 2 deals with development of suitable electrical resistance (ER) measuring methods. Subproject 3 is responsible for comparative studies on corrosion rate measured by different electrochemical techniques, ER and weight loss coupons. Subproject 4 is concerned with electrochemical methods and data transfer with GSM SMS. In subproject 5 microbiological activities are measured and related to the observed corrosion rate. In subproject 6 the results from the mentioned five subprojects are combined in designing a test rig for in-situ corrosion measurements. Each of the subprojects will be presented in the following with their backgrounds, activities and obtained results.

Subproject 1 Characterisation of sulphur compounds and examination of their effects with respect to corrosion

Responsible: Tor Hemmingsen, Stavanger University College
Co-workers: Nils Aagotnes, Stavanger University College
Torfinn Havn, Aker Offshore Partner
Ivar Austvoll, Stavanger University College
Erling Skavås, Stavanger University College
Frederik Fusek¹³, Stavanger University College

Background

The presence of sulphur compounds causes a sulphide film to be formed on a carbon steel surface. This film is conductive and may cause an increase in the corrosion rate. It is therefore important to get an understanding of how sulphide or sulphur oxide compounds react with a steel surface, and what factors are important for the rate of this reaction.

Electrochemical methods like cyclic voltammetry can be used in order to determine the reaction scheme for the sulphur compounds. The formation of a black sulphide film can easily be visually observed, and by monitoring the film formation the reaction rate can be determined. The relative rate of film formation can be followed optically in a galvanic set-up where two steel samples are exposed to two different electrolytes. The monitoring of the galvanic current will also give information of which electrolyte is most corrosive.

¹³ Post.doc student, on leave from Comenius University, Bratislava, Slovakia

Activities

The project started in April 2001 and has been promoted by two papers authored by participants in the project and published in the Danish Chemical Society journal "Kemi", the Norwegian Chemical Society journal "Kjemi" and in "Euroheat & Power". The project has been presented on the Stavanger University College web site <http://imn.ux.his.no>, for the main purpose of attracting MSc students to the project. The project is presented at Norwegian Corrosion Technical Society and Norwegian Chemical Society in Stavanger and Danish Corrosion Technical Society and Denmark Technical University in Copenhagen.

Hemmingsen, with the assistance of engineers at the department, has done electrochemical experiments on sulphur compounds chemistry. Also, a Ph.D. student from Iceland, Sonja Richter, has been a visiting researcher doing research on the cyclic voltammetry of sulphur compounds. The results of the analytical part in fresh water are fairly similar to the results obtained in artificial seawater. A Ph.D. student scholarship financed through Stavanger University College has been attached to this project.

A sabbatical year from teaching 2002-03 for Tor Hemmingsen included a research stay at Denmark Technical University. The research in collaboration with Lisbeth Hilbert and Lars Vendelbo Nielsen was focused on monitoring film formation combined with ER-measurements in water purged with hydrogen sulphide. Dr. Ivar Austvoll from Stavanger University College was connected to the project in order to make a data program in MatLab which could analyse the video sequences which was obtained from the monitoring of the electrodes. Ph.D. student Erling Skavås was connected to the project in February 2003, and has worked mainly with cyclic voltammetric experiments on sulphur compounds at different pH values. He has concentrated his work so far to analyses of sulphur compounds using a Rotating Ring Disk Electrode (RRDE). In March 2004 he has made analyses on site of district heating waters at Iceland. He will continue his PhD-work for 6 months with wall jet electrodes in Gent University, Belgium from September 2004. In October 2003 Post.doc Frederik Fusek, on leave from Bratislava University started his optical film formation experiments combined with electrochemical measurements for different sulphur compounds at a range of pH values.

Results

Sulphur compounds like sulphite, dithionite and even sulphide have been used for years as oxygen scavengers in injected seawater to increase oil production offshore or in feed water for distribution systems in district heating onshore. In correct concentrations they act in accordance with their purpose – that of removing oxygen - while the ions themselves are oxidized to sulphate. However, it has been known in the last decades that excessive dosing of sulphur-based oxygen scavengers will produce sulphide ions. This may result in very corrosive conditions, and a black iron sulphide film may be observed. Results from previous work have shown that the film formed is dependent on the environmental conditions, and that such film may undergo transformation over time. The films have both different structures and different electrochemical potentials, and may therefore be cathodic or anodic when they are in contact with a metal.

In this work the purpose was to monitor the film formation by the use of video cameras in parallel with corrosion measurements by the use of ER and galvanic techniques. Since the water in most

district heating systems is alkaline to minimize corrosion, the work in this study focuses on alkaline electrolytes. Sosa et al. have examined sulphide film formation in alkaline brine, but little has been done in fresh water systems. The solubility of hydrogen sulphide and its corresponding anions is given in Fig. 4.1.1 and shows clearly that the hydrogen sulphide concentration increases dramatically above pH 7.

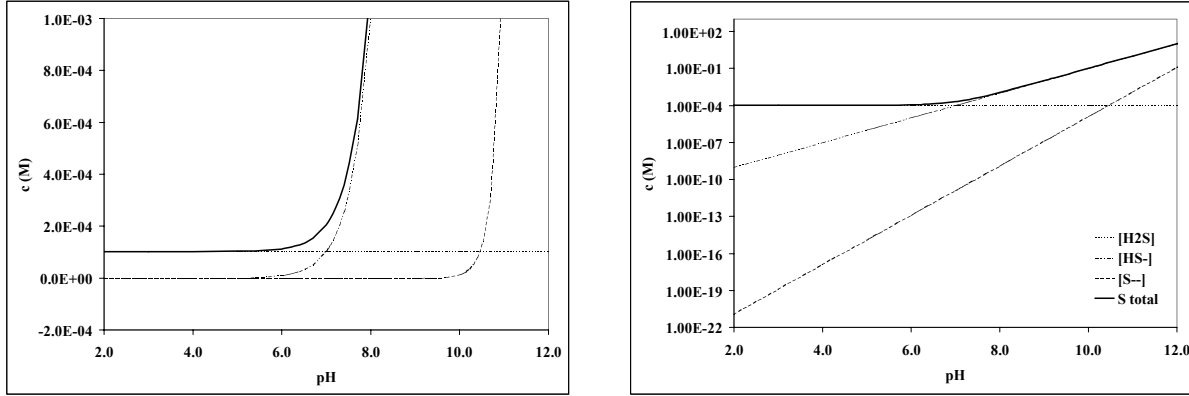


Fig. 4.1.1. Effect of pH on solubility of hydrogen sulphide and its corresponding anions in water in 1000 ppm H₂S gas atmosphere.

The exposure of steel in a hydrogen sulphide environment leads to the formation of a black ferrous sulphide film. The rate of film formation is initially a 2-dimensional process which proceeds in a 3-dimensional process. However, it is found that at low concentrations or at a low anodic polarisation, 3-dimensional growth starts before the monolayer is complete.

Hydrogen sulphide is an acid and dissociates in water to form hydrogen ions and hydrogen sulphide or sulphide ions. As proposed by Shoesmith et al. hydrogen sulphide can be adsorbed on steel and oxidised. The adsorbed, oxidised hydrogen sulphide can react to form mackinawite or ferrous ions as shown in Equations 1-4.



The activity of ferrous and sulphide ions and the pH has a strong effect on which film modification is formed initially and how it reacts further. Mackinawite (FeS) is the primary product at pH values from 6.5 to 8.8. Ferrous ion activity can be high in an acidic environment due to high corrosivity and low sulphide activity. This will lead to porous deposits, whereas the opposite will be the case in alkaline media. Newman et al. have shown that the history of the deposits has a profound effect on the later passivation properties. Passivation occurs rapidly if bare steel is exposed to a high sulphide concentration with low concentrations of ferrous ions in the solution. However, carbon steel with a porous ferrous sulphide film formed in low concentrations of sulphide or with an oxide film formed in oxygenated seawater will not be able to form a protective film in high concentrations of sulphide at a later stage.

The formation of a heterogeneous biofilm on the surface creates very diverse conditions and thereby concentration gradients of oxygen, hydrogen sulphide and pH. These gradients represent an accelerating force that can lead to the formation of corrosion cells.

A rig was constructed for measuring film formation by electrochemical and optical measurements. The lower cabinet compartment was equipped with four cameras (two in use in the experiments) and an artificial light source. The light was turned on for 10 seconds in sequences of 10 minutes. The recording sequences of four cameras were triggered by the ignition of light, and 30-second video sequences were stored in an mpeg format. A separate data program, made in MatLab, could extract single pictures 5 seconds into each recorded sequence. The pictures were analysed with respect to grey tone, and presented as histograms. Optionally, the extracted pictures could be transferred to a film sequence in order to visualize the film formation reaction.

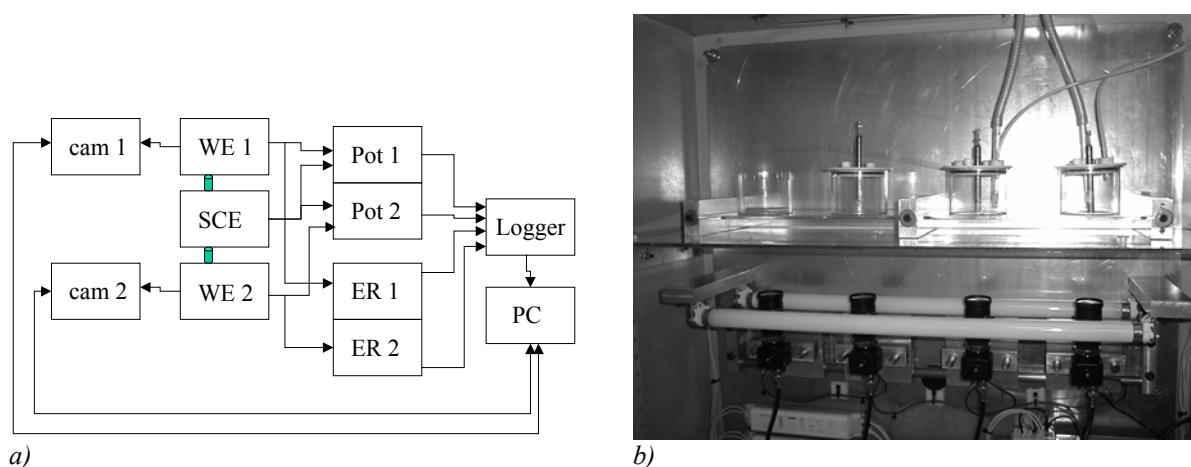


Fig. 4.1.2. a) A schematic set-up of the equipment. b) Four cells in cabinet with cameras. Cables to the electrodes are not included on the photo.

Two carbon steel ER probes formed as horseshoes, cf. Fig. 4.1.4, were exposed to phosphate-buffered electrolytes at pH 7.00 or pH 9.35 under an atmosphere of 0, 50 or 1000 ppm hydrogen sulphide mixed with nitrogen. Most experiments were run for 2 days while the potentials, current at open circuit potential (OCP), and electrical resistance were measured.

An experiment was run with ER probes in phosphate-buffered electrolytes at pH 7.00 and pH 9.35 in equilibrium with 50 ppm hydrogen sulphide gas atmosphere. No sulphide film was formed at pH 7.00 while a loose thin black sulphide film was formed at the electrode at pH 9.35. The potentials of the probes stabilized at -700 mV in pH 7.00 and -770 mV SCE in pH 9.35 as shown in Fig. 4.1.3a. The thickness changes of the ER probes gave corrosion rates of 2 $\mu\text{m}/\text{year}$ in pH 7.00 and 4 $\mu\text{m}/\text{year}$ in pH 9.35 at the end of the experiments.

Experiments were also run in a 1000 ppm hydrogen sulphide atmosphere. A denser black sulphide film was formed at the electrode at pH 9.35 compared with the lower hydrogen sulphide concentration. The ER measurements stabilized at 10 $\mu\text{m}/\text{year}$ at pH 9.35 under a hydrogen sulphide atmosphere and decreased to 5 $\mu\text{m}/\text{year}$ under a preservative nitrogen atmosphere over the next 24 hours, while a stable OCP current of 0.1 μA was obtained through the complete period, see Fig. 4.1.3b. A complete overview of the results is given in Table 4.1.1.

Table 4.1.1. A summary of the results with reference to potentials (mV SCE), ER corrosion rates ($\mu\text{m}/\text{year}$) and galvanic currents (nA) in presence of hydrogen sulphide.

Rates (mA/cm ²) and galvanic currents (mA) in presence of H ₂ O ₂ or salicide.														
Cell 1		E		ER		Cell 2		E		ER		I		
Gas	pH	24	end	24	end	Gas	pH	24	end	24	end	24	end	
1	50	7.00	-747	-744	5.5	4.4	50	9.35	-787	-787	4.7	2.0	36	42
2	1000	7.00	-744	-719	7.3	4.4	1000	9.35	-838	-821	8.0	1.5	91	100
3	50	7.00	-742	-725	14.6	14.2	50	9.35	-843	-834	8.0	13.4	100	110
4	0	9.35	-794	-642	16.4	16.4	50	9.35	-844	-823	12.0	4.4	-47	-83
5	0	7.00	-745	-586	36.5	3.7	50	7.00	-745	-731	22.3	9.1	0	-147
6	50	9.35	-856	-599	2.6	76.7	50	9.35	-856	-717	2.4	1.0	0	-119

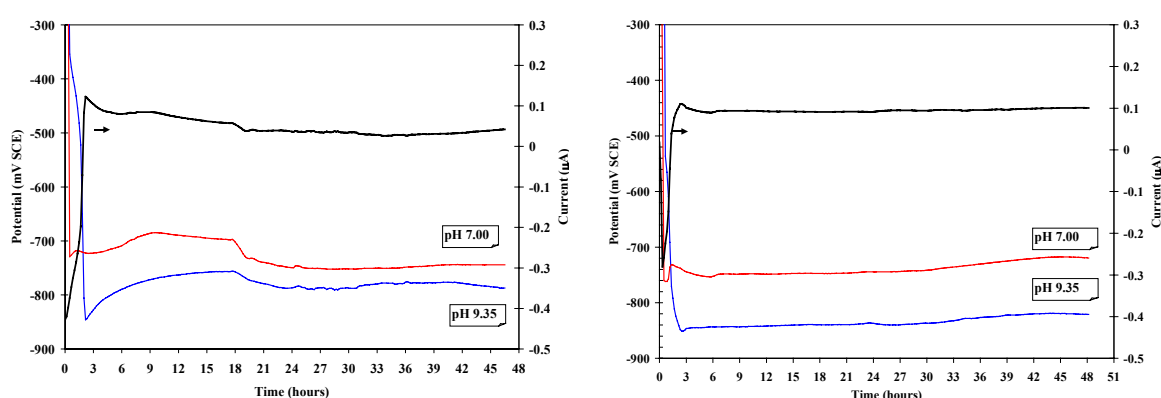


Fig. 4.1.3. The potentials for ER probes and the currents between the ER probes ($R=1\text{ Mohm}$) in pH 7.00 and pH 9.35 under a) 50 ppm and b) 1000 ppm hydrogen sulphide atmosphere.

Analogue experiments were run with the ER probes at pH 7.00 and 9.35 in a 50 ppm hydrogen sulphide atmosphere where aerated water or thiosulphate were added. No dramatic changes were observed except for the periods when the addition was made. On the other hand, when free air access was allowed at the end of the experiment, the film on the electrode in the cell at pH 9.35 turned from cathodic to anodic, see Fig 4.1.4a, and the corrosion rate from ER measurements increased considerably.

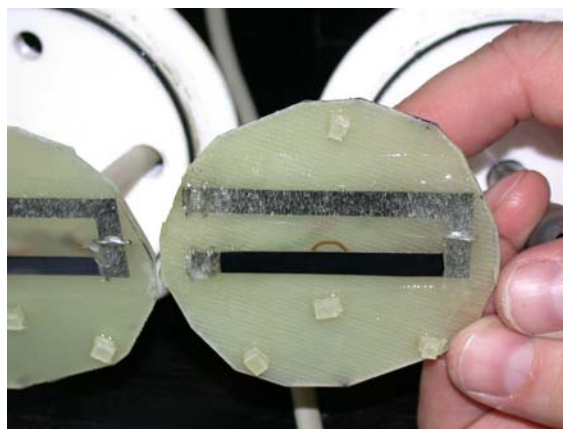
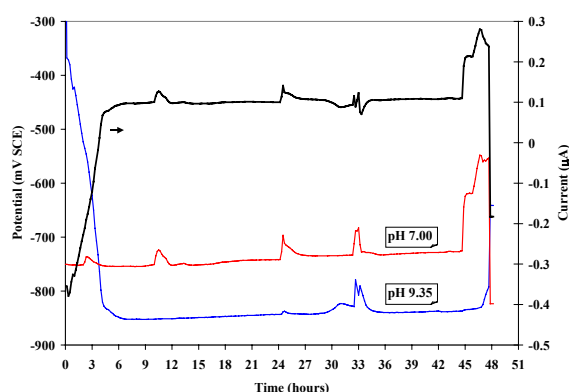
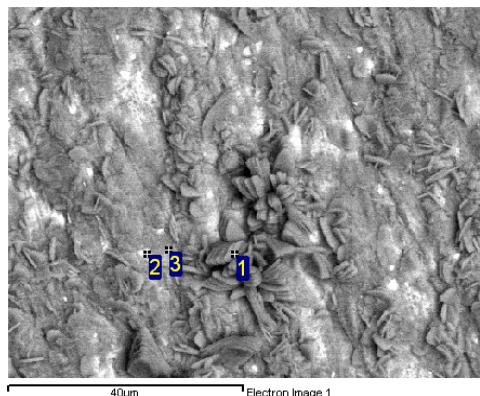


Fig. 4.1.4. a) The potentials and the currents between the ER probes ($R=1\text{ Mohm}$) in pH 7.00 and pH 9.35 under 50 ppm hydrogen sulphide atmosphere with addition of aerated water or thiosulphate. b) Photo of the ER probes after 48 hours at pH 9.35.

In order to compare the effect of added and non-added sulphide, two ER probes were galvanically coupled in electrolytes at pH 9.35 under a 50 ppm hydrogen sulphide atmosphere and under a nitrogen atmosphere. An iron sulphide film was formed on the surface, but only a very small OCP current was obtained and the potential was stable at -850 mV.



Element analyses of spots marked in the electron microscope picture gives the following composition:

Spot	P	S	Mn	Fe
1	19.44	0.31		80.25
2	0.48	0.29	1.26	97.97
3	10.54	5.15		84.31

Fig. 4.1.5. Area of ER probes exposed to pH 7.00 in 50/1000 ppm hydrogen sulphide atmosphere. SEM picture with EDAX-spot analyses of the surface given as weight percentage of elements.

An examination of the corroded electrode surfaces showed that iron phosphate precipitates on the bare steel surface, and combined iron phosphate and iron sulphide products can be found where a sulphide film is formed as shown in Fig. 4.1.5. The potentials are low, showing that the iron surface is active. This is in contradiction to potentials at 0.1 V SCE for a phosphate inhibited carbon steel surface, which is found by Harms et al.

An 11-day experiment was therefore run in order to see the effect of phosphate at pH 9.35 in 50 ppm hydrogen sulphide atmosphere in a buffered and non-buffered electrolyte. No significant corrosion could be observed in the first 3-day period, and the potential was stable at approximately -850 mV during that period. After 78 hours the potential increased on both electrodes to -730 mV and -630 mV for the phosphate and hydroxide based electrolytes, respectively, and the corrosion rate of the electrode in hydroxide increased significantly, as shown in Fig. 4.1.6a. A lag time before corrosion attacks of approximately 3 days is in accordance with results found in other experiments at pH 8.5 in 50 ppm hydrogen sulphide atmosphere. Also the ER measurements showed a significant increase in the corrosion rate, as shown in Fig. 4.1.6, with values of 76 and $1 \mu\text{m}/\text{year}$ in the hydroxide and the phosphate electrolyte, respectively. The addition of thiosulphate after 100 hours gave a new increase in potentials, most dominant in the hydroxide electrolyte, and thus a higher anodic OCP current for the hydroxide exposed electrode. However, the added thiosulphate did not seem to cause a change in the corrosion rate. After 11 days a dense protective iron sulphide film was formed on the electrode in a phosphate-buffered electrolyte, while a non-complete sulphide film with pitting was seen on the electrode in a black-coloured hydroxide electrolyte, see Fig. 4.1.6b.

Grey tone analyses from video sequences taken every 10 minutes are Fig. 4.1.7a and shows that after 60 minutes a 2-dimesional film growth starts, which proceeds as a 3-dimensional film growth after approximately 6 hours as shown in Fig. 4.1.7b.

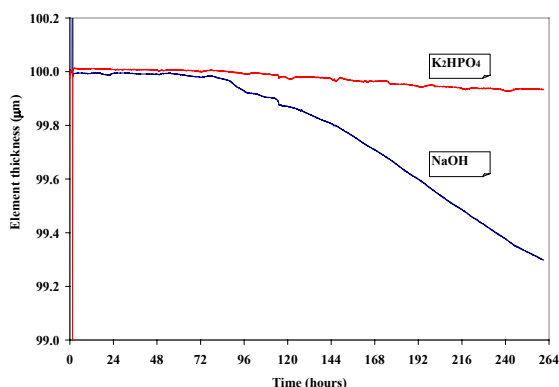


Fig. 4.1.6. a) The element thickness of ER probes pH 9.35 (in 25 mM K₂HPO₄ or 22 mM NaOH) is under 50 ppm hydrogen sulphide atmosphere in an 11 day experiment with b) photo of the electrode exposed to 22 mM NaOH (50x).

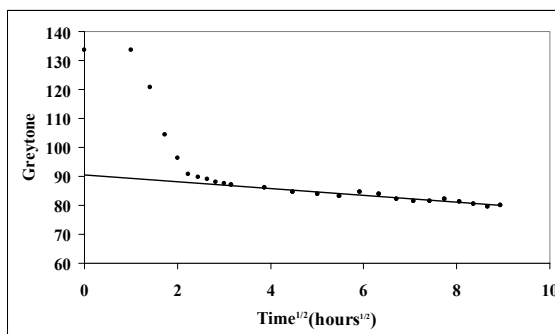
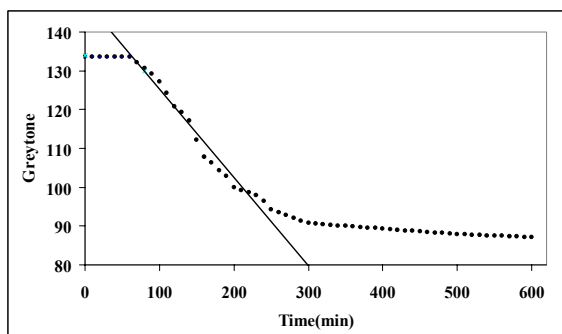


Fig. 4.1.7. a) Grey tone analyses of ER probes at pH 9.35 in 22 mM NaOH under 50 ppm hydrogen sulphide atmosphere.

Sulphur compounds may exist in many oxidation states, sometimes as a mixture. Fig. 4.1.8 shows an overview of the most important sulphur and sulphur oxides present in an aqueous solution.

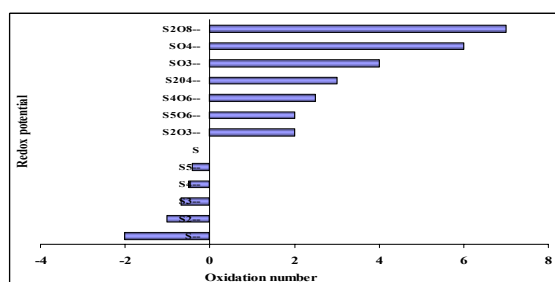
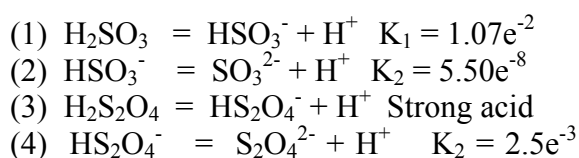


Fig. 4.1.8. Sulphurs oxidation number

Cylindrically formed carbon steel electrodes with sides embedded into epoxy were made for doing electrochemical/optical experiments for sulphite and dithionite.

In Table 4.1.2 potential results are presented for corrosion current monitoring for 2-days experiments in presence of sulphite and dithionite.

Table 4.1.2. An overview of potentials and corrosion rates after 50 hours exposure time for experiments run in distilled water, 10 mM sulphite or 10 mM dithionite at various pH-levels.

	pH 3		pH 5		pH 7		pH 9	
	E/V	i / μ A	E/V	i / μ A	E/V	i / μ A	E/V	i / μ A
Distilled water	-660	4,9	-778	1,0	-790	0,45	-800	0,19
Sulphite	-725	45	-735	45	-755	30	-805	20
Dithionite	-720	60	-715	55	-750	10	-820	2,0

The corrosion process was monitored by video cameras in sulphite electrolytes simultaneous with corrosion rate measurements, while pictures were taken after the 70-hours' experimental period. Fig. 4.1.9 shows that the darkest film is formed at pH 3 and 5, while on the electrode exposed to pH 9 only a thin film is observed. The reason for these differences is most probably due to lower dissolution rate of iron, which could react with the sulphite during formation of iron sulphide.

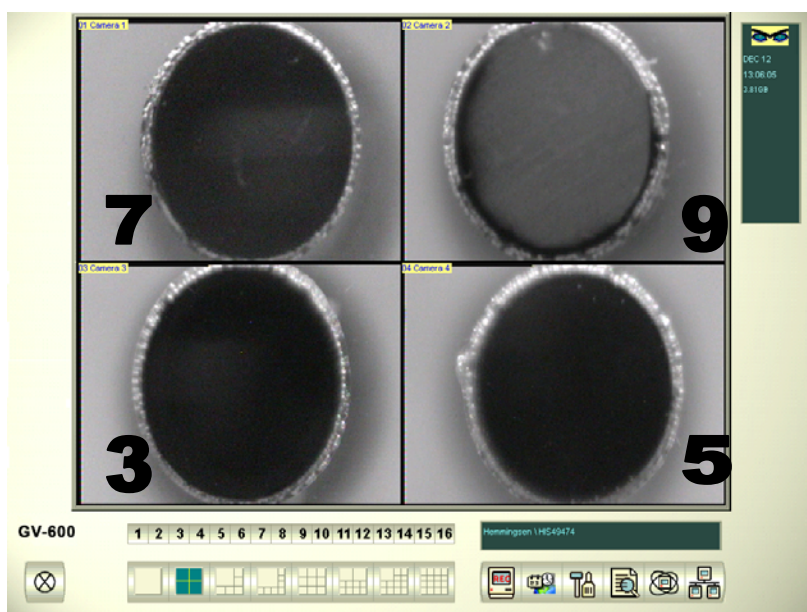


Fig. 4.1.9. Pictures from electrodes exposed to 10 mM sulphite for 70 hours. Camera 1 at pH = 7, camera 2 at pH = 9, camera 3 at pH = 3, and camera 4 at pH = 5.

In order to analyse the different sulphur and sulphur oxide compounds cyclic voltammetric sweeps were done on rotating ring-disk platinum electrodes combined with a bipotentiostat. In Fig. 4.1.10 cyclic voltammetric sweeps on platinum is shown for electrolytes with different concentrations of sulphite. A linear dependence between current response and sulphite concentration could be found for a range of potentials, and a plot for the concentration range 5-100 mM at a potential of 750 mV SCE is shown in Fig. 4.1.12. Dithionite responds on a wider potential range as shown in Fig. 4.1.11,

and thus, interferes with sulphite on the higher potentials. A combined analysis is shown in Fig. 4.1.13 at a potential of 350 mV SCE, where sulphite is added to a dithionite electrolyte.

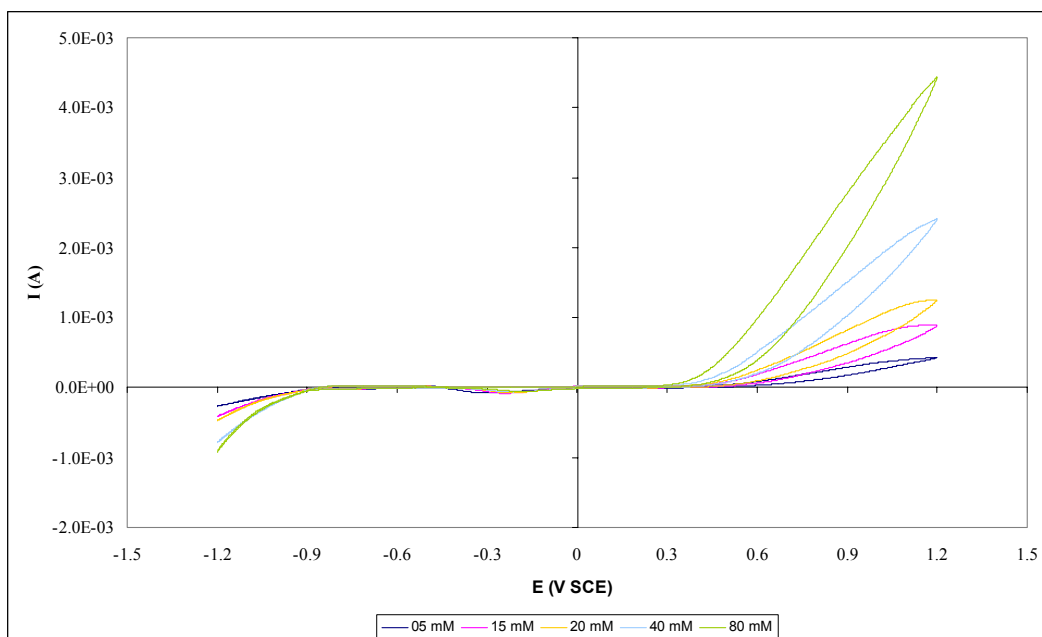


Fig. 4.1.10. Cyclic voltammetric sweep for 5-80 mM sulphite at pH 11 at 1000 rpm rotation rate.

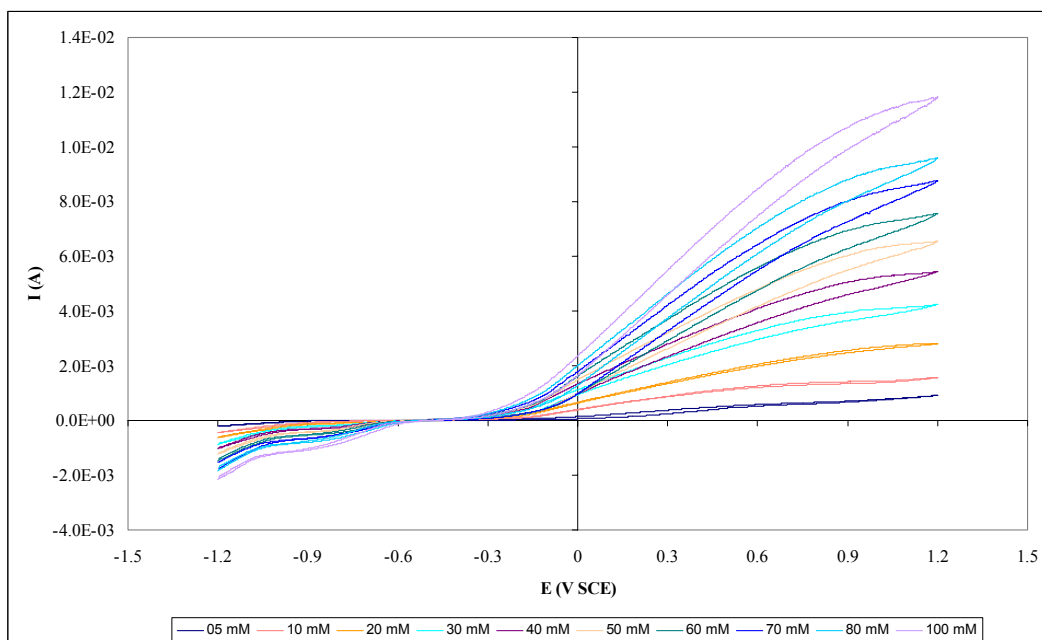


Fig. 4.1.11. Cyclic voltammetric sweep for 5-100 mM dithionite at pH 11 at 1000 rpm rotation rate.

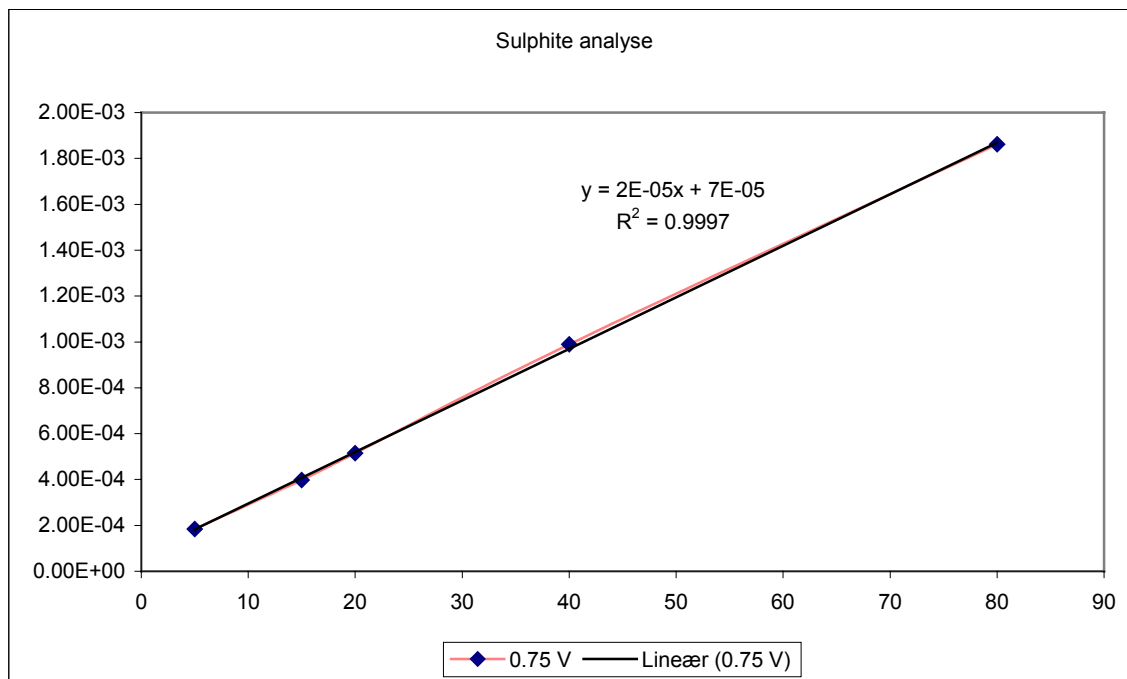


Fig.4.1.12. Current response at 750 mV SCE in cyclic voltammetric sweep for 5-80 mM sulphite at pH 11 at 1000 rpm rotation rate.

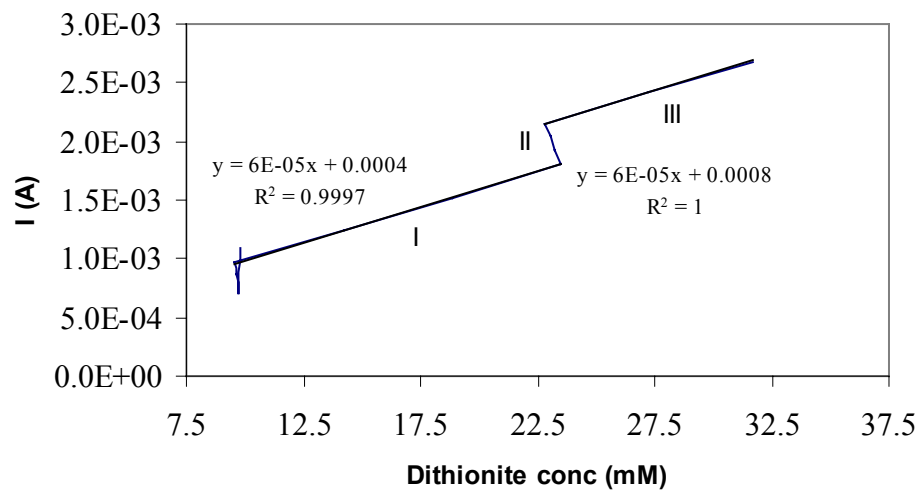


Fig. 4.1.13. Current response at 350 mV SCE in cyclic voltammetric sweep at pH 11 at 1000 rpm rotation rate for combined addition of sulphite and dithionite.

A solution with a 10 mM dithionite concentration is added 0 to 30 mM sulphite in 5 mM steps, which can be seen as minor potential changes in the very beginning of the curve in Fig. 4.1.13. The dithionite concentration on the x-axis is corrected due to a volume increase when a concentrated sulphite solution is added. Then dithionite is added in steps until 23.5 mM (region I), and the

current raises with a linear slope of 65 $\mu\text{A}/\text{mM}$ dithionite at an applied potential of 0.35 V SCE. A new addition of sulphite until 46.1 mM (region II) is followed by a stepwise addition of dithionite to 54.3 mM (region III), and an identical slope for the current increase is achieved.

Both dithionite and sulphite show a linear current response at a potential of 750 mV, and for dithionite also at a potential of 350 mV, but with inference of sulphite. Compensation from measurements at a lower potential may be useful for concentration determinations when both dithionite and sulphite are present.

More details of the work are given in papers, see:

1. Hemmingsen, T., Hilbert, L., Nielsen, L.V., Assessment of sulphur and H_2S corrosion by the use of simultaneous ER, galvanic and optical measurements. Presented at Eurocorr 2003 in Budapest, Hungary, September 2003.
2. Hemmingsen T., Austvoll I., Fusek F. and Skavås E.: Combined optical and electrochemical measurements on sulphide film formation. Presented at 13th Scandinavian Corrosion Congress, Reykjavik, Iceland, April 2004.

Conclusions and recommendations

- ER-probes will be useful measuring instruments for monitoring corrosion in low conductive and low-corrosive water in district heating systems.
- Optical measurements by cameras with data converted to grey level analyses is a good tool for monitor the film formation, and might be installed in a by-pass loop for a district heating system.
- Cyclic voltammetric measurements give information of the reactions of e.g. sulphur compounds in district heating water.
- An adapted scan procedure on platinum electrodes can be used to follow specific sulphur compounds, but this method has to be refined.
- Combining these and other techniques may give powerful tools to monitor the process in flow lines for heating water.

Future plans

The project has been and is presented on the WEB site, <http://imn.ux.his.no>, at Stavanger University College. A Ph.D. student scholarship is financed through Stavanger University College, and Erling Skavås was employed as a Ph.D. student in a research field related to this project in February 2003. The employment will end in 2006. Assistant professor in image analysing, Ivar Austvoll, at Stavanger University College has recently been involved in this research.

Post.doc. Frederik Fusek will have a 12-month stay from October 2003. He is from Bratislava and has been funded by NATO fellowships in order to do research within this project.

During Tor Hemmingsens stay as a visiting researcher at The Technical University of Denmark joint research with L.V. Nielsen and L. Hilbert was done on optical measurements combined with ER-measurements on carbon steel electrodes exposed to hydrogen sulphide in fresh water, see paper 1. A new test-rig with camera set-up was made in Stavanger and financed through this project, and future collaboration in this field is foreseen. A continuation of this activity is also combined with use of a new multiplexed potentiostat. A stereomicroscope with an electrochemically flow-cell is under construction for studies of kinetics of sulphide film formation. Ph.D. student Erling Skavås will have a research stay in Belgium from September 2004 for further studies with a wall jet technique.

Subproject 2 ER-technology for district heating systems

Responsible: Lars Vendelbo Nielsen, MetriCorr
Co-workers: Kaj Vendelbo Nielsen, MetriCorr
Lisbeth R. Hilbert, DTU

Background

The purpose of the project is to improve the quality control in district heating systems by corrosion monitoring. The recommended Danish water quality includes a low conductivity, negligible oxygen content and pH values of approximately 9.8, which ideally leads to the formation of a protective layer of magnetite. Local destabilisation of the magnetite layer caused by precipitation of deposits may lead to localized under-deposit corrosion that accelerates by even a small ingress of oxygen.

Subproject 2 focuses on development of a high-sensitive ER-sensor for district heating purposes. The sensor should be able to make a fast detection of very low general corrosion rates as well as detection of localized under-deposit corrosion. The sensor should be tested in comparison with various electrochemical techniques as described in sub-project 3, and designed to fit into the unit for corrosion monitoring designed by Force Technology (described in sub-project 6). Accordingly, the sensor should be able to provide corrosion rates for subsequent correlation with the chemical parameters provided by the separate portable panel being part of the corrosion monitoring unit design by Force Technology (sub-project 6).

Activities

- A. The establishment of design criteria by setting up basic algorithms for resistance change versus corrosion rate has been completed as a pre-project activity and the algorithms subsequently used for designing the district heating ER-probe in the present project.
- B. Pre-project modifications of the transmitter/excitation and the receiver/amplifier circuitry has resulted in considerably enhanced measurement resolution and consequently considerably lowered the time needed to establish instant corrosion rate.
- C. The ER-probe was designed and manufactured in accordance with the criteria resulting from calculations using the basic algorithms, and subsequently tested with respect to temperature response in oil bath and response when exposed in low-corrosive waters.
- D. The temperature response of the probe was studied by exposing the probe in thermostatically controlled oil bath and measuring reference element resistance as well as differential resistance as a function of the temperature in the temperature interval 20-80°C.
- E. The response in low-corrosive water was established in a preliminary laboratory test using the Force Technology unit for corrosion monitoring and associated separate panel for chemical measurements. Measurements were e.g. compared with electrochemical

impedance measurement performed using three electrode arrangements designed and manufactured by DTU as part of sub-project 3.

- F. Laboratory comparative evaluation of the ER concept with InterCorr International SmartCET equipment.
- G. Studies on film formation in the presence of hydrogen sulphide. During a research visit at the Technical University of Denmark by Dr. Tor Hemmingsen (Stavanger University College - responsible for sub-project 1), MetriCorr participated in studies on film formation in the presence of hydrogen sulphide. A new four-camera set-up was built by Stavanger University College in order to optically monitor the film formation in parallel with Electrical Resistance (ER) measurements and galvanic measurements of electrodes exposed to different environmental conditions. The results are presented in sub-project 1.
- H. Field tests in various district heating plants.
- I. A comparative field study between the ER concept, The Force LOCOR Cell, and the InterCorr International SmartCET equipment has been performed in Odense Kommunale værker.
- J. A comparative field study between the ER concept and the InterCorr International SmartCET equipment has been performed in Iceland and is reported in sub-project 3.

Results and Discussion

A. Design-criteria, basic algorithms

The ER-technique utilizes that the electrical resistance in a metal plate increases when the plate suffers from metal loss due to corrosion.

For a metal plate with dimensions as illustrated in Fig. 4.2.1, the electrical resistance of the plate (as a function of plate thickness, σ , and temperature, T) can be described by:

$$R(T, \sigma) = \rho(T) \cdot \frac{L}{W \cdot \sigma} \quad (1)$$

where $\rho(T)$ is electrical resistivity of the metal element.

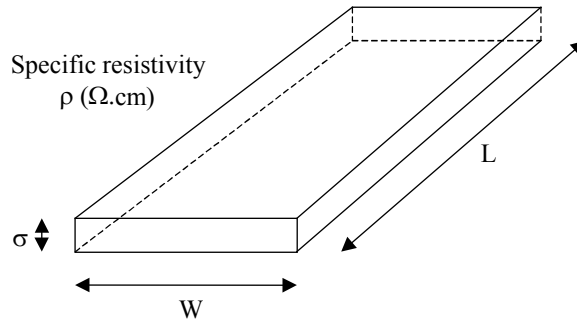


Fig. 4.2.1. Schematic illustration of dimensions of metal plate used in calculations of electrical resistance according to equation (1).

The electrical resistivity of a metal depends on temperature. Literature data¹⁴ for pure iron suggests that resistivity can be approximated into a linear relation in the temperature range 0 -130°C. The approximation can be expressed as:¹⁵

$$\rho(T) = 0.06 \cdot T / ^\circ \text{C} + 8.43 \quad (10^{-8} \Omega \cdot \text{m}) \quad (2)$$

The relation between corrosion rate and increase in resistance (dR/dt) can be expressed:

$$V_{\text{corr}} = \frac{dR}{dt} \cdot \frac{K}{R^2} \quad (3)$$

Where,

$$K = \rho(T) \cdot \frac{L}{W} \quad (4)$$

Hence, the corrosion rate of the metal plate can be estimated by measuring co-ordinate values of dR/dt and R .

The above equations can be used for assessment of response time for a given set of parameters (V_{corr} , ΔR (measurement resolution), L/W , σ , $\rho(T)$) according to:²

$$\Delta t = \frac{\Delta R}{V_{\text{corr}}} \cdot \frac{W}{L} \cdot \frac{\sigma^2}{\rho(T)} \quad (5)$$

This formula has been used for design criteria for the probe. Correlations between corrosion rates measured by the ER concept have been compared with controlled anodic current response and mass loss measurements.²

¹⁴ Handbook of Chemistry and Physics, D.R. Lyde (Ed.). 75th edition, CRC Press Inc., 1994.

¹⁵ Measurement of accumulated corrosion and instant corrosion rate using a new differential electrical-resistance technique, K.V. Nielsen and L.V. Nielsen, VN-Instrument Technical Paper (1998).

B. Modifications of circuitry

Fig. 4.2.2 (right) shows the principle of the modified high sensitive electrical resistance (ER) technique for corrosion rate measurement as compared with traditional measuring circuitry for accumulated mass loss measurements (left). A particular feature of this modified technique is the capability of providing a direct measure of the difference between exposed element C and reference element R by an amplifier (A3 in Fig. 4.2.2). Differential measurement is achieved by returning excitation current to ground in midpoint between exposed element C and reference element R.

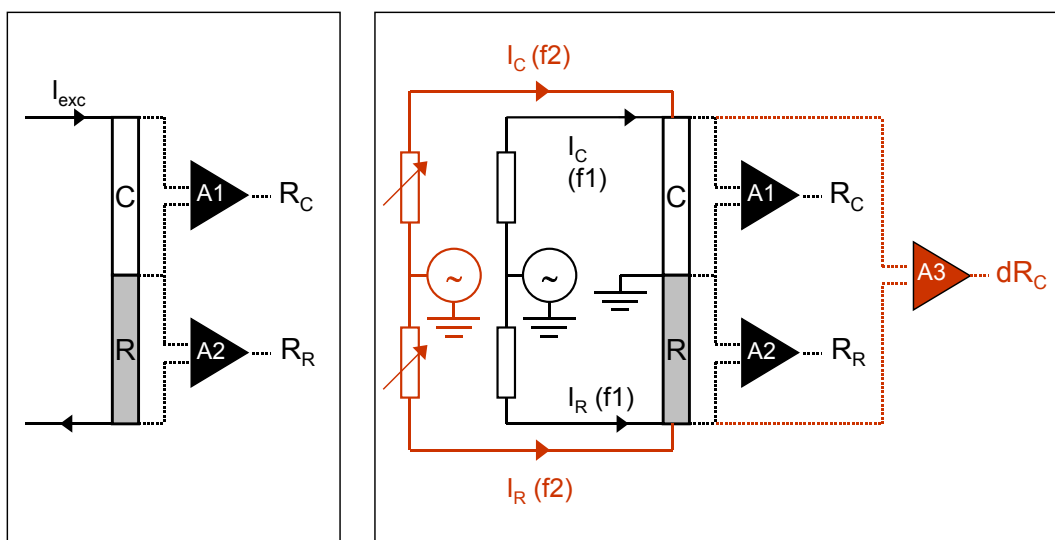


Fig. 4.2.2. Traditional ER measuring circuit (left) and modified high-sensitive circuit (right).

A very high resolution in dR_C is obtained by keeping the dynamic range in an interval of a few milliohms interval via possibility of asymmetrical adjustment of the excitation current flowing across the exposed element and the reference element.

C. Probe design and manufacturing

A probe with a reference- and an exposed element was manufactured in accordance with principles of the above differential, high-sensitive ER concept. Elements were made from 100 μm thick iron foil.

In district heating systems in Denmark, the general corrosion rate is usually low. The probe was designed to give information on corrosion rate in the region of 1-2 $\mu\text{m}/\text{y}$ within 24 hours. Using equation (5), element dimensions ($L=200\text{mm}$, $W=2\text{mm}$, and $\sigma=0.1\text{ mm}$) give a resistance increase of 4 $\mu\Omega/\text{day}$, which is about 40 times instrument resolution. These element dimensions were accordingly chosen for the district heating system (DHS) ER probe. Fig. 4.2.3 is a photo of the probe prototype. The fish-shaped symmetric element holder ensures minimal effect of thermal expansion on resistance measurements, and allows for theoretical behaviour of the element impedance as well as the differential impedance when temperature alters.



Fig. 4.2.3. DHS ER-probe design.

D. Temperature response

Fig. 4.2.4 shows resistivity measurements as a function of the temperature, and Fig. 4.2.5 shows data converted into resistivity in comparison with the tabulated values.

The resistivity for the element material can be described by:

$$\rho(T)/10^{-8} \Omega \cdot m = 0.051 \cdot T / ^{\circ} C + 10.11 \quad (6)$$

The data in Figs. 4.2.4-5 in combination with equations (3) and (4) gives the following correlation between corrosion rate and dR/dt at 60°C:

$$V_{\text{corr}} (\mu m/y) = 7.0 \cdot \frac{dR}{dt} (\mu \Omega/h) \quad (7)$$

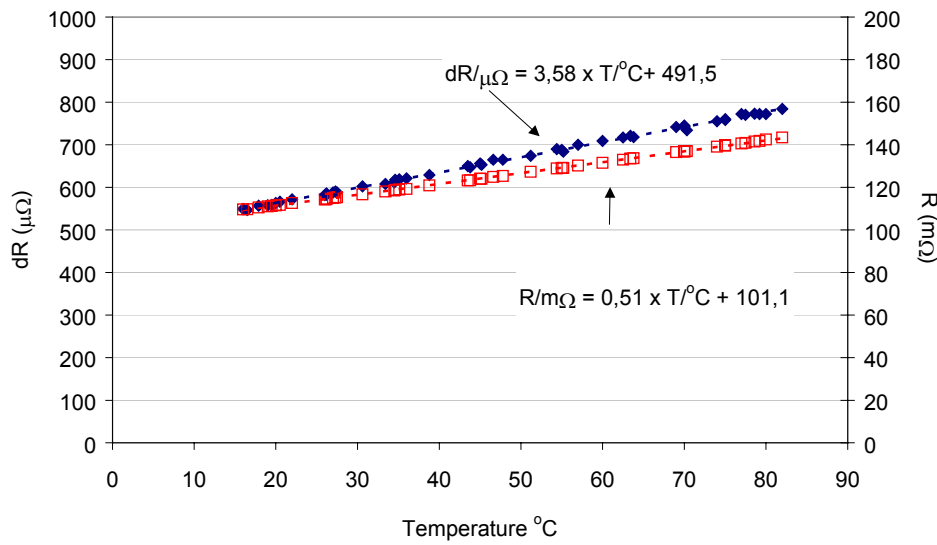


Fig. 4.2.4. Reference element resistance and differential resistance as a function of temperature.

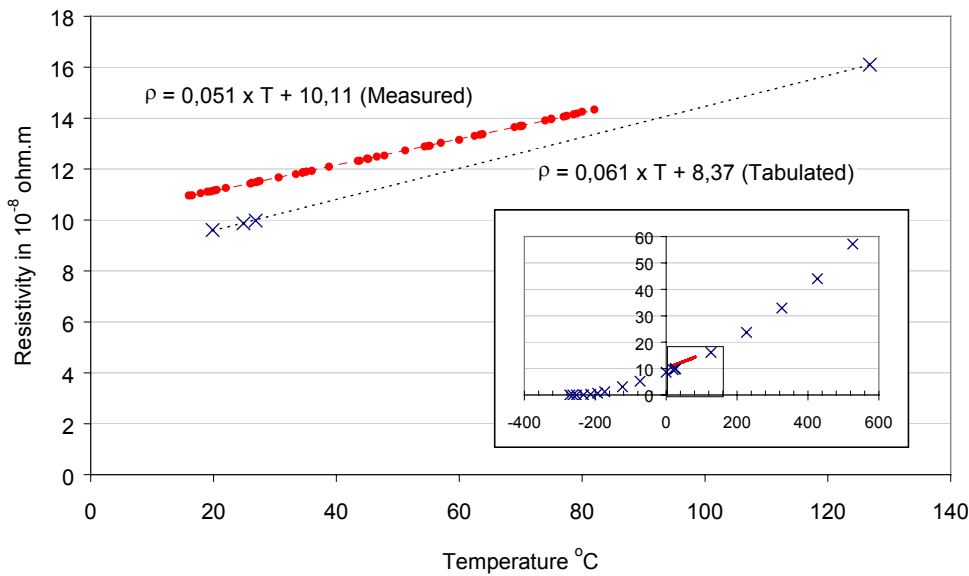


Fig. 4.2.5. Resistivity of element material.

In general, ER technology for corrosion measurements needs to rely on proper means for temperature compensation. The reference element resistance should provide such means since this element resistance depends solely on temperature. In traditional ER concepts, the reference element resistance should be a well-defined function of the temperature, as should the exposed element resistance in absence of corrosion. Hence, the temperature compensation algorithm, leading to the temperature compensated exposed element resistance $R_{C,comp}$ may be as described by equation 8:

$$R_{C,comp} = R_C(T) \cdot \frac{R_R(T_0)}{R_R(T)} \quad (8)$$

Where, $R_C(T)$ is measured exposed element resistance at actual temperature T , $R_R(T_0)$ is reference element resistance at reference temperature T_0 , $R_R(T)$ is measured reference element resistance at actual temperature T . Fig. 4.2.6 shows differential resistance as a function of the element resistance (data from Fig. 4.2.4).

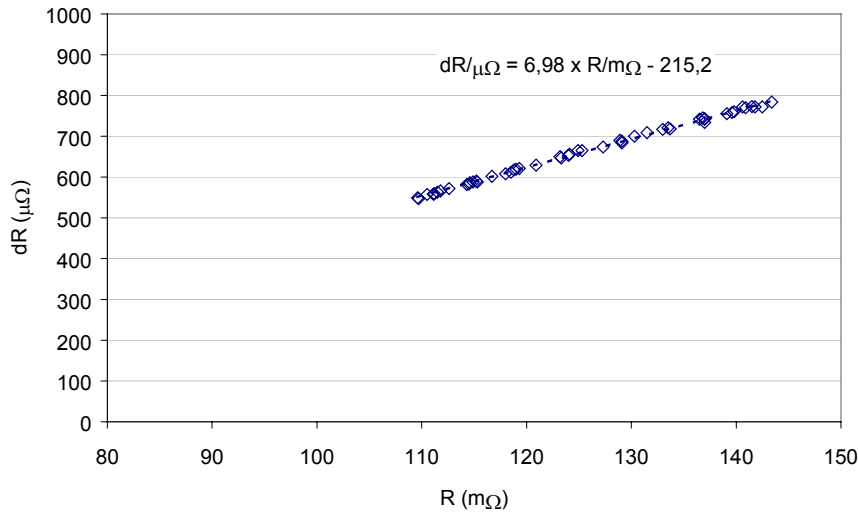


Fig. 4.2.6. Differential resistance as a function of reference element resistance in the temperature range 20-80°C.

Temperature response data presented in Fig. 4.2.6 show that the above temperature compensation algorithm is applicable in exact same manner for the differential resistance dR_C , hence giving temperature compensated differential resistance $dR_{C,comp}$ according to the algorithm:

$$dR_{C,comp} = dR_C(T) \cdot \frac{R_R(T_0)}{R_R(T)}$$

Where, $dR_C(T)$ is measured differential resistance at actual temperature T . Since differential impedance can be adjusted prior to the measurement to a value chosen by the operator, the temperature effect at dR_C adjusted to zero is eliminated without algorithmic assistance.

E. Response in low-corrosive waters

Fig. 4.2.7 shows example of response from the ER probe throughout a 1-hour test period during which the high-sensitive ER technique was actively recording the differential resistance. The probe was positioned in the unit for corrosion monitoring designed by Force Technology. From the slopes of the curves the corrosion rate was calculated ($1.7 \mu\text{m/y}$).

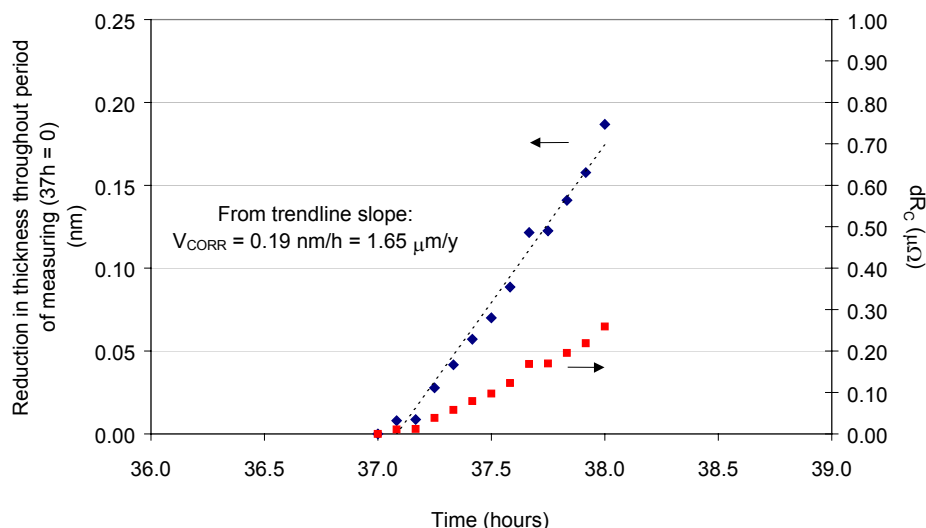


Fig. 4.2.7. ER-probe response in district heating water quality.

Comparison with EIS measurements were performed in simulated district heating water quality (diluted borax buffer) conductivity $20 \mu\text{S/cm}$, temperature 60°C at two different initial pH values (series A: pH = 8.3 and series B: pH = 9.5).

In both series, the simulated district heating water was purged with (1) nitrogen, (2) nitrogen + 5% air, (3) nitrogen + 15% air, and (4) nitrogen + 40% air.

Results are shown in Fig. 4.2.8, illustrating that low corrosion rates are obtained regardless of pH and oxygen content. Some differences between EIS and ER are evident, however, both showing low corrosion.

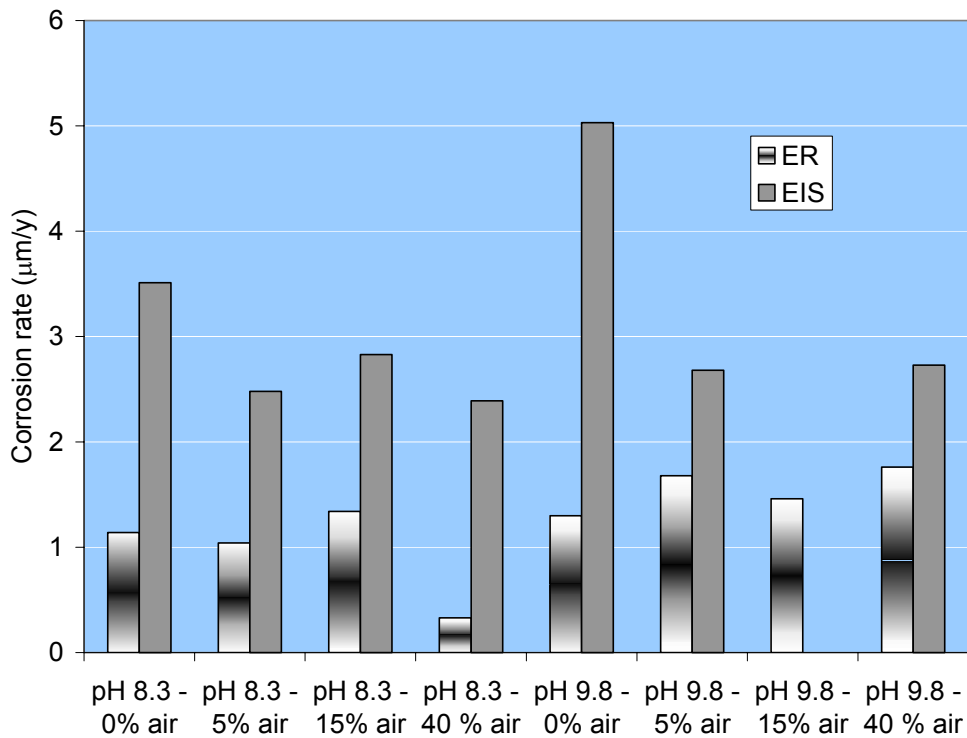


Fig. 4.2.8. Results from ER and EIS comparison in simulated district heating waters.

F. Laboratory comparative evaluation of the ER concept with InterCorr SmartCET equipment

A comparative laboratory study of the performance of InterCorr SmartCET and MetriCorr ER technique has been performed. SmartCET is a multi-electrochemical technique, online, real-time corrosion monitoring device. It includes automated LPR for general corrosion measurement, HDA for assessment of B value (Stern-Geary constant) for refinement of the corrosion rate, and electrochemical noise (EN) for assessment of pitting tendencies

Besides SmartCET- and ER measurements, electrochemical impedance (EIS) measurements were performed at the end of the test periods.

Experiments were conducted in a 2-liter glass vessel equipped as a three-electrode cell. In the studies, the ER sensor element used for the laboratory measurements acted as the working electrode in a three electrode setup used for the SmartCET survey. In this manner, corrosion at the exact same electrode was simultaneously detected by both instrumentations. The working electrode was a MetriCorr ER probe with carbon steel element dimensions (length x width x thickness) 100 x 2 x 0.1 mm (total area 2 cm²). Counter- and reference electrodes were identical carbon steel plates with dimensions (length x width x thickness) 100 x 30 x 2 mm (total area 60 cm²) – Fig. 4.2.9. Usually, it is recommended by InterCorr that the SmartCET measurements are made on three identical electrodes, and the procedure used in this study do not for this reason fully comply with recommended optimum conditions for the SmartCET.



Fig. 4.2.9. Electrodes used for the studies.

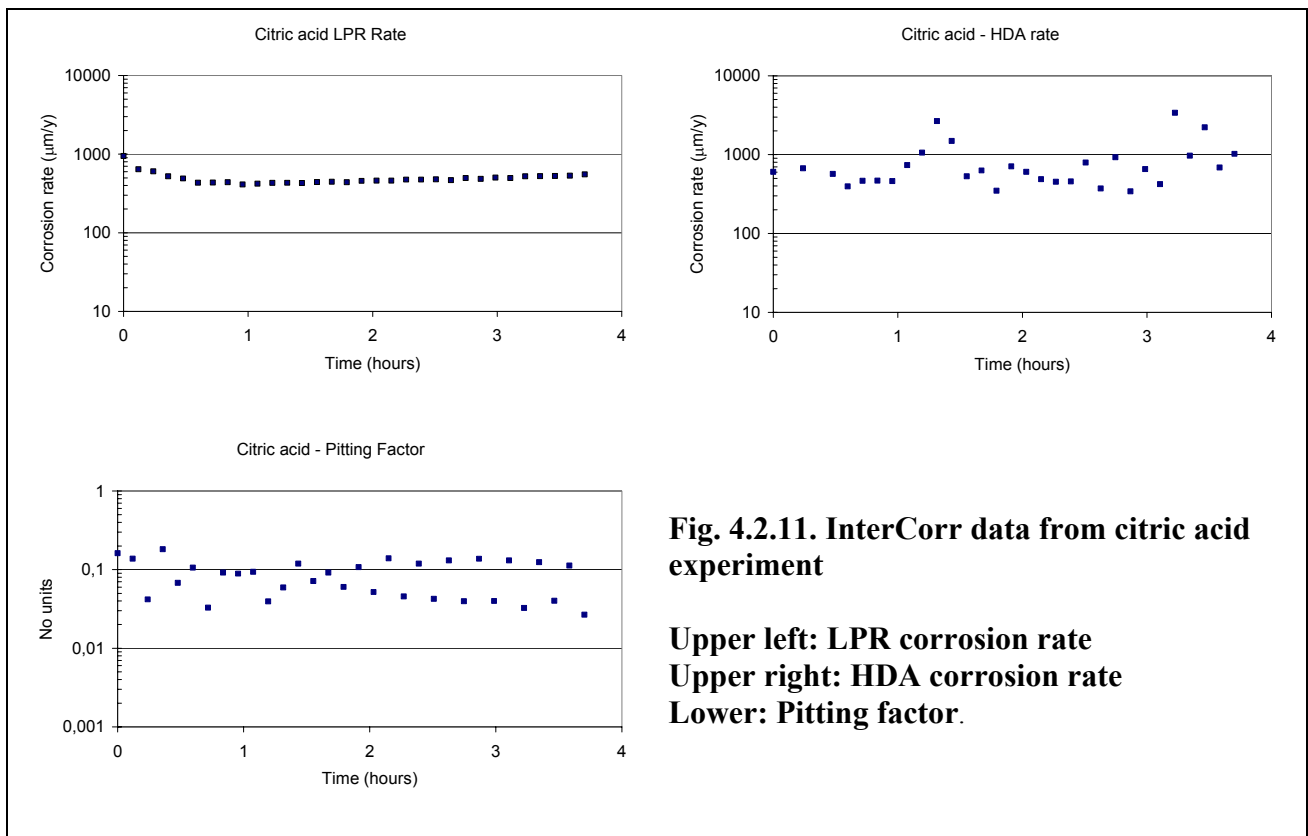
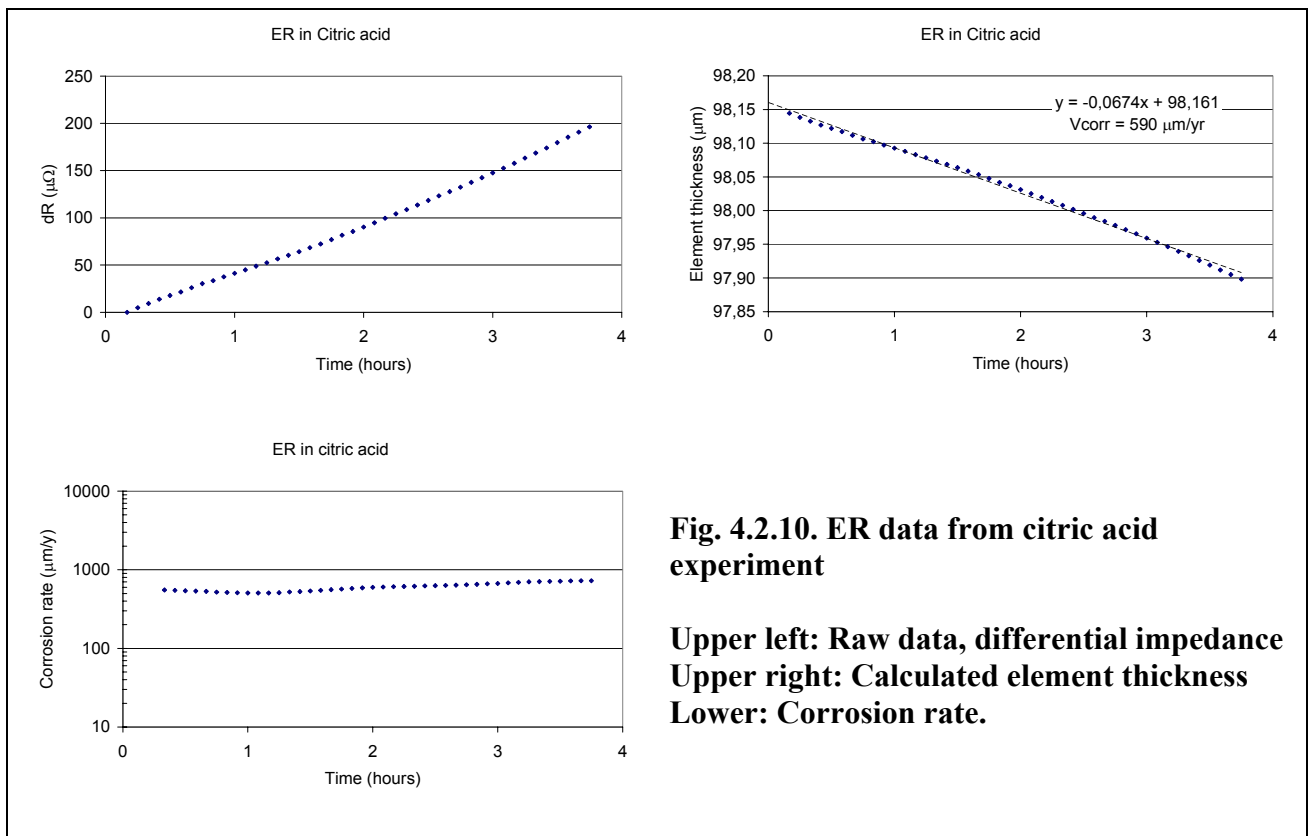
The experiments were conducted in three different environments in agreement with suggestions by Dave Eden (InterCorr International):

1. High corrosivity. Citric acid (5%) in water (pH = 2.2, conductivity = 5.3 mS/cm. Duration app. 4 hours.
2. Moderate general corrosivity. Using aerated 3% brine (pH = 6, conductivity = 50 mS/cm). Aeration via a glass frit. After about 10 hours, the aeration had stopped and was re-established. Total duration app. 18 hours.
3. Low corrosivity. Sodium Nitrite inhibited water containing ~ 100 ppm nitrite, and < 100 ppm chloride. In practice; Danish tap water (pH = 7.7, conductivity = 0.8 mS/cm); after 24 hours 100 ppm nitrite in the form of NaNO_2 was added. Total duration app. 90 hours, however, since ER measurements were stopped after some 64 hours due to datalogger troubles, the InterCorr data in this report are presented for this amount of time as well.

The experiments were made for a screening purpose, and no coupons were employed to evaluate the direct mass loss – this should be incorporated in future direct comparative experiments.

Besides SmartCET- and ER measurements, electrochemical impedance (EIS) measurements were performed (using the same electrode configuration) to complete (at the end of) the tests. Frequency range 10 kHz – 10 mHz, and amplitude 10 mV.

Results are plotted in Figs. 4.2.10-18. ER measurements in the form of differential impedance, calculated element thickness, and real time corrosion rate calculated from slopes of the differential impedance. SmartCET measurements in the form of LPR rate, HDA rate and pitting factor. EIS measurements are presented in the form of Nyquist- and Bode-plots (Figs. 4.2.16-18).



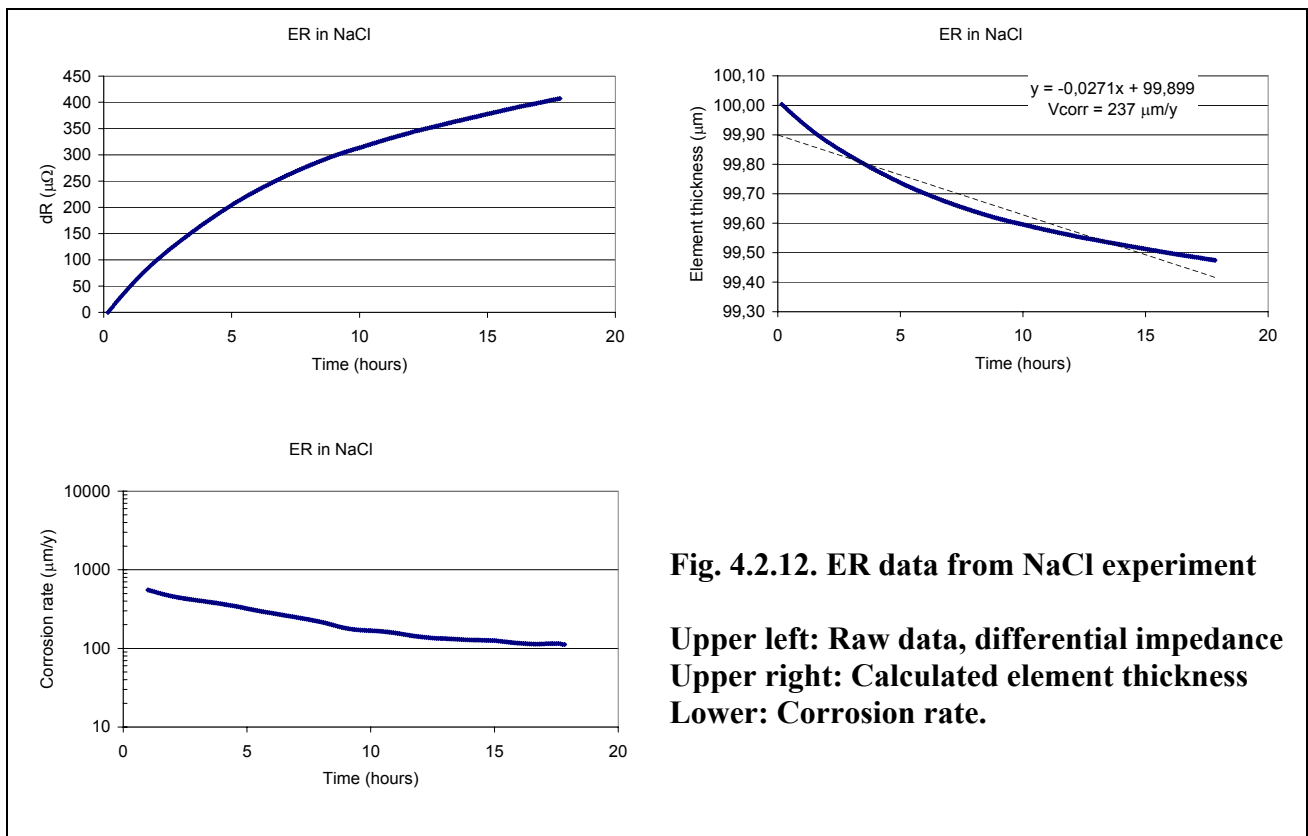


Fig. 4.2.12. ER data from NaCl experiment

**Upper left: Raw data, differential impedance
Upper right: Calculated element thickness
Lower: Corrosion rate.**

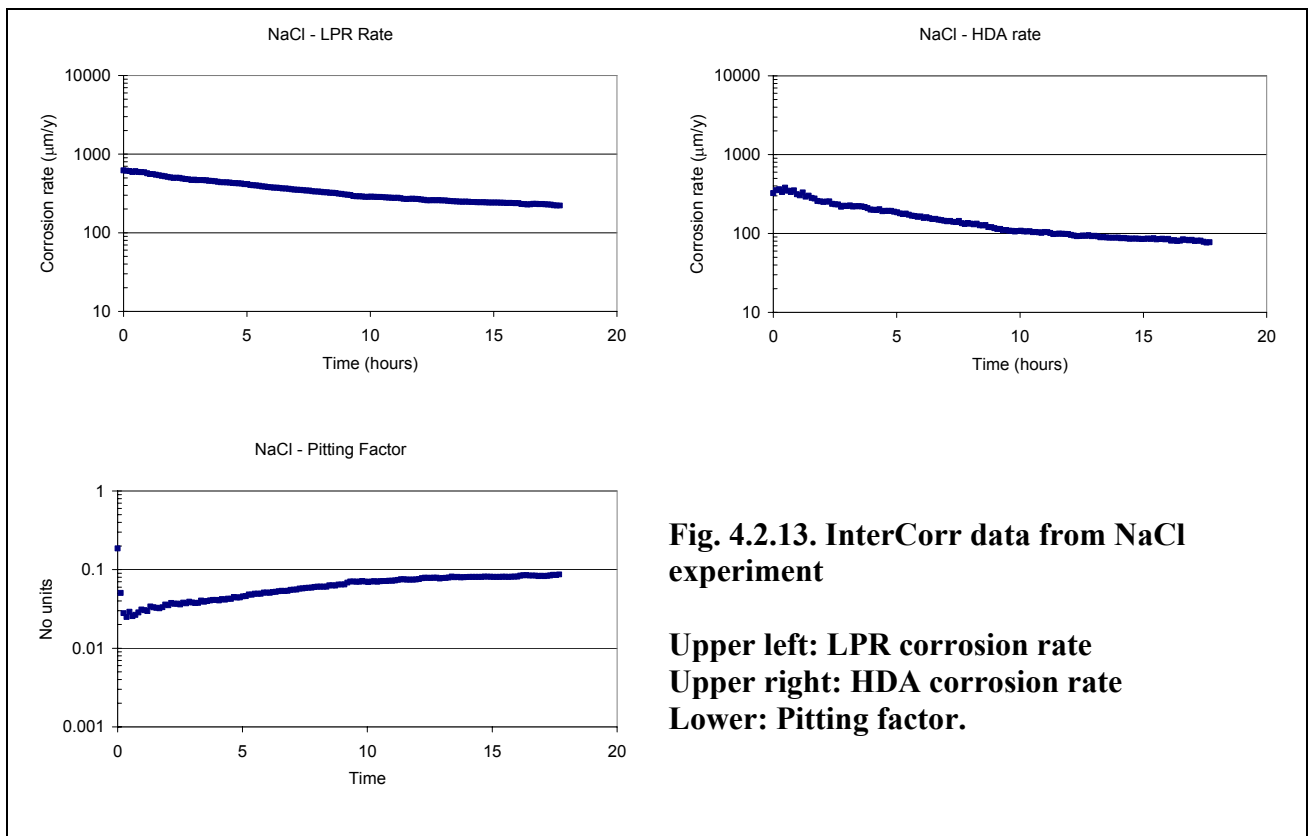
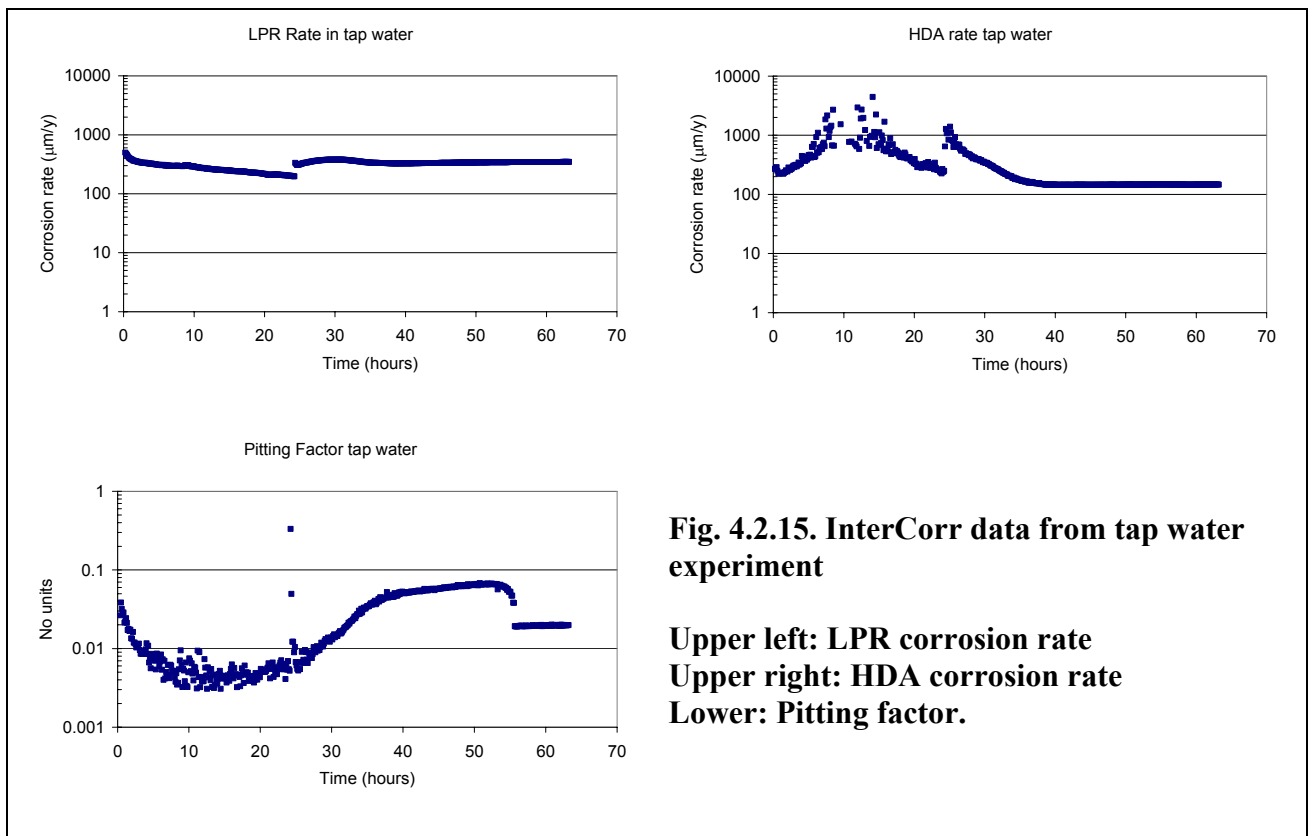
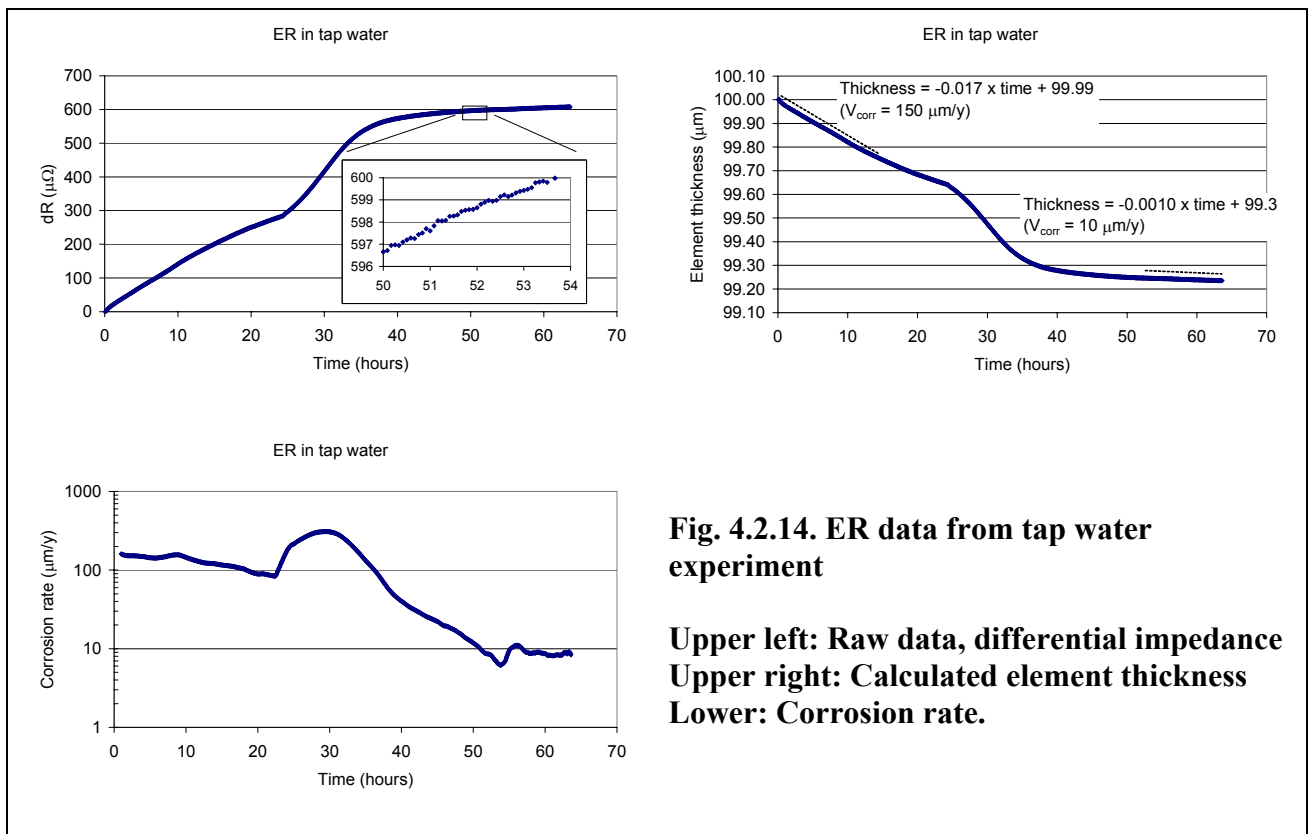


Fig. 4.2.13. InterCorr data from NaCl experiment

**Upper left: LPR corrosion rate
Upper right: HDA corrosion rate
Lower: Pitting factor.**



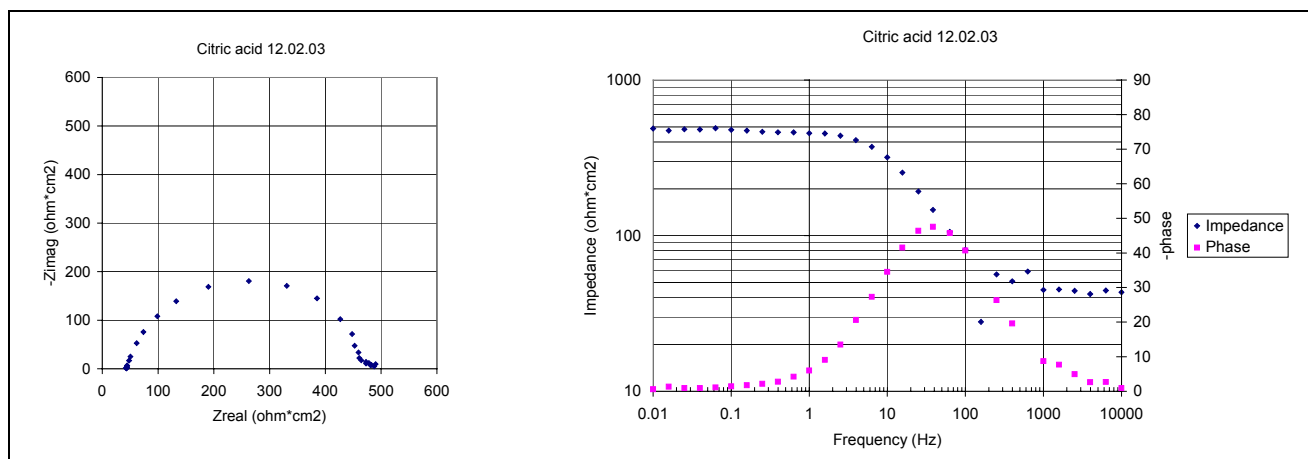


Fig. 4.2.16. Nyquist- (left) and Bode plot (right) for EIS measurement performed at the end of the citric acid experiment.

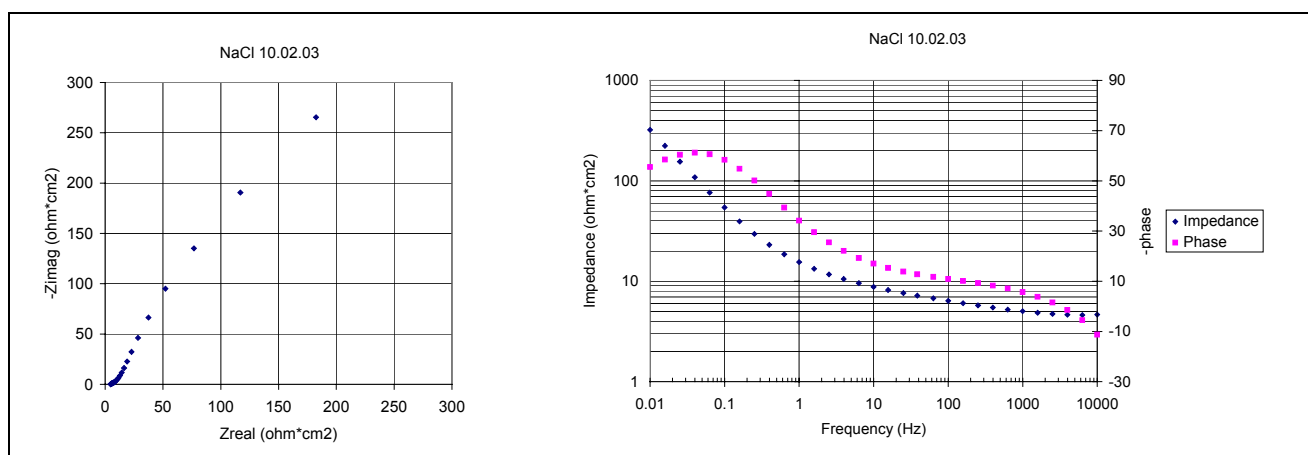


Fig. 4.2.17. Nyquist- (left) and Bode plot (right) for EIS measurement performed at the end of the brine experiment.

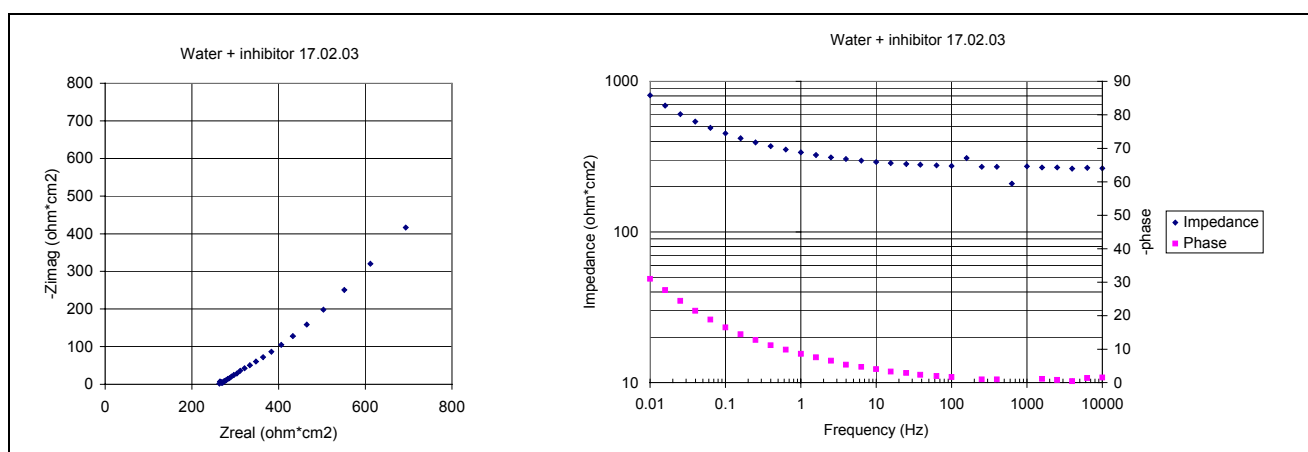


Fig. 4.2.18. Nyquist- (left) and Bode plot (right) for EIS measurement performed at the end of the tap water experiment.

The interpretation (applied equivalent circuit and related physical quantities) of the EIS measurements is assembled in table 4.2.1.

Table 4.2.1. EIS equivalent circuits and calculated quantities (by Lisbeth Rischel Hilbert, DTU).

Solution	Eq. circuit	R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	Q1	n1	R3 ($\Omega \cdot \text{cm}^2$)	Q2	n2
Citric acid	R(RQ)	42	365	2.8E-05	1	-	-	-
Brine	R(Q(R(RQ)))	4.5	11.7	3.5E-04	0.8	3400	7.3E-03	0.6
Inh. tap W	RQ	260	-	5.6E-03	0.4	-	-	-

In the citric acid experiment, both ER (Fig. 4.2.10) and LPR/HDA (Fig. 4.2.11) detects a high corrosion rate. The experiment was completed after 4 hours.

The ER measurement define a corrosion rate of 590 $\mu\text{m}/\text{y}$ in average, and due to the relatively large increase in differential impedance, the corrosion rate in this case can be calculated from slopes from one measurement to the next (5 minute intervals). Initial and final values are tabulated in table 4.2.2.

LPR measurements range from 550 – 950 $\mu\text{m}/\text{y}$, and the HDA is in the same order of magnitude, however, perhaps with a certain appearance of scatter that may be caused by the hydrogen bubbles formed in the process. Initial- and final data from the LPR and HDA are tabulated in table 4.2. The agreement with the ER measurements is very good.

The EIS data define a nice semicircle with well-defined polarization resistance corresponding 830 $\mu\text{m}/\text{y}$.

The brine experiment was allowed to run for about 18 hours.

The ER measurement integration period was 1 hour (Fig. 4.2.12). The average ER corrosion rate was found to be 240 $\mu\text{m}/\text{y}$, ranging from initially 550 $\mu\text{m}/\text{y}$ to finally 110 $\mu\text{m}/\text{y}$.

The LPR- and HDA rates (Fig. 4.2.13) are quite identical, however, both correlating very well with the ER, and with the HDA indicating 80 $\mu\text{m}/\text{y}$ at the final stages.

EIS define a non-completed semicircle behavior, which can be fitted as defined in table 4.2.1. Corrosion rate based on (R2+R3) is calculated to be 90 $\mu\text{m}/\text{y}$ – in good agreement with both ER, LPR and HDA.

The tap water experiment was continued for some 90 hours, but only the first 65 hours reported here due to datalogger problems regarding the last part of the ER-measurements. Nitrite inhibitor was added after 24 hours.

The ER rate prior to inhibition was around 100 $\mu\text{m/y}$, and the immediate effect of the nitrite is an increase up to 300 $\mu\text{m/y}$ in peak value, after which the corrosion rate decays to around 10 $\mu\text{m/y}$. Resolution in the region of 0.1 $\mu\Omega$ is indicated in Fig. 4.2.17.

The LPR and HDA measurements also showed increased corrosion subsequent to the nitrite addition. LPR rate, however, stays higher and a steady state of 350 $\mu\text{m/y}$ continues after inhibitor addition. The HDA rate stabilizes at 150 $\mu\text{m/y}$.

EIS measurements show a long diffusion tale (Fig. 4.2.18), and no corrosion rate has been assessed from this.

All initial and final corrosion rate values are tabulated in table 4.2.2 and visualized in Fig. 4.2.19.

Table 4.2.2. Corrosion rates.

Solution	ER initial $\mu\text{m/y}$	ER final $\mu\text{m/y}$	LPR initial $\mu\text{m/y}$	LPR final $\mu\text{m/y}$	HDA initial $\mu\text{m/y}$	HDA final $\mu\text{m/y}$	EIS final $\mu\text{m/y}$
Citric acid	550	725	950	550	680	1000	830
Brine	550	110	620	220	390	80	90
Tap water	150 (un-inh)	10 (inh.)	400	350	240	150	? (diffusion)

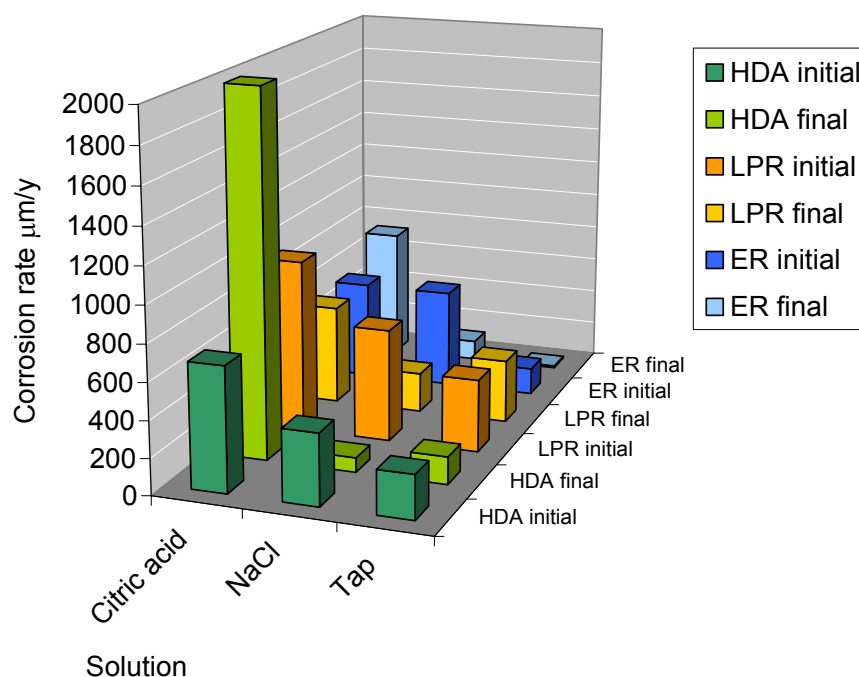


Fig. 4.2.19. Graphical presentation of measured corrosion rates.

G. Studies on film formation in the presence of hydrogen sulphide.

- Please refer to report from sub-project 1.

H. Field tests in various district heating plants.

MetriCorr personnel have been responsible for installation and operation of the equipment for field tests in Denmark. Besides a preliminary test program in Ballerup local heating system, field tests have now been completed in 6 industrial plants. Please refer to the report from sub-project 6.

I. A comparative field study between the ER concept, the Force LOCOR cell, and the InterCorr SmartCET equipment.

These tests were performed at Odense kommunale værker, Næsbyhoved Broby (local plant) in the period December 13th 2002 to February 26th 2004. During this period of time, weight loss coupons were exposed. In the period January 13th – February 19th 2003 intensified electrochemical and ER measurements were conducted.

The district heating system in Odense is constructed as a linked system of local plants (Fig. 4.2.20), each of which equipped with boilers for heating of the water as well as facilities for additions of make up water.

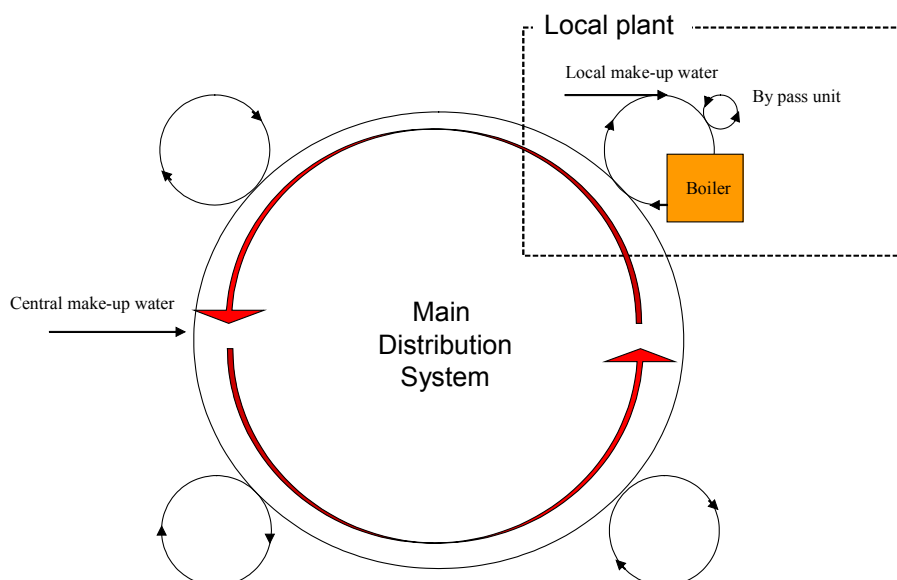


Fig. 4.2.20. Sketch of the District heating system in Odense, Denmark.

The Næsbyhoved Bobby (NB) plant where the survey was performed is one such local plant. The survey was utilizing the by pass unit described in sub-project 6. In this unit, a separate panel for oxygen, pH and conductivity measurements was mounted (figs 4.2.21-24).

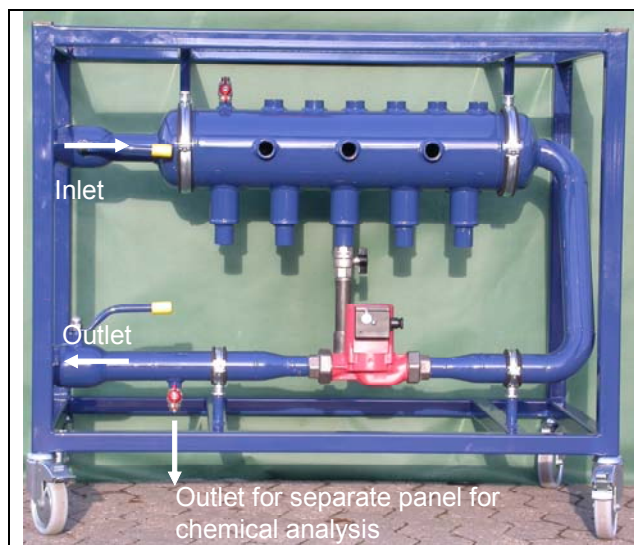


Fig. 4.2.21. The side stream unit with chamber for probe positioning.

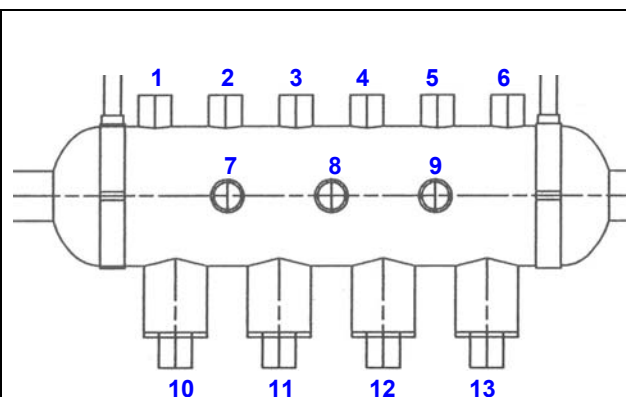


Fig. 4.2.22. Outline of the access fitting configuration.

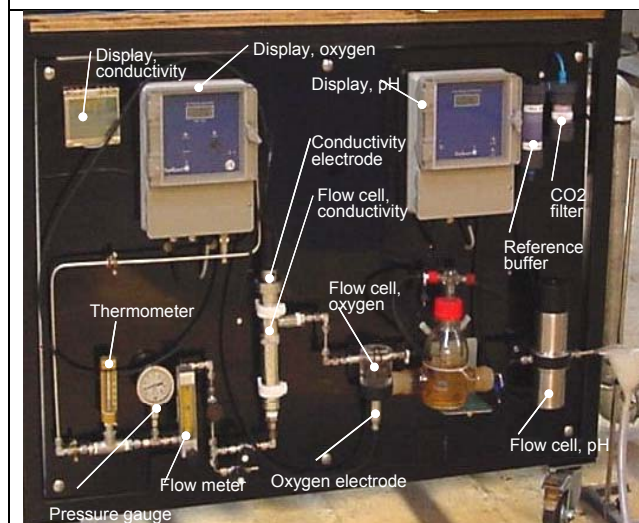


Fig. 4.2.23. Separate panel for oxygen, pH and conductivity measurements.



Fig. 4.2.24. Panel mounted on side stream unit during operation.

Various probes of carbon steel were positioned in the by pass unit (Figs. 4. 2.25-28), including:

- Weight loss probes.
- Three-electrode probes (area of each electrode 9.4 cm^2).
- A LOCOR[®] cell which can be used to measure galvanic current between pipe wall and a carbon steel anode placed behind a glass frit in the cell.
- ER probes (200 x 2 x 0.1 mm)



Fig. 4.2.25. Weight loss coupon. (Force Technology).



Fig. 4.2.26. Three-electrode probe for electrochemical measurements. (Technical University of Denmark).

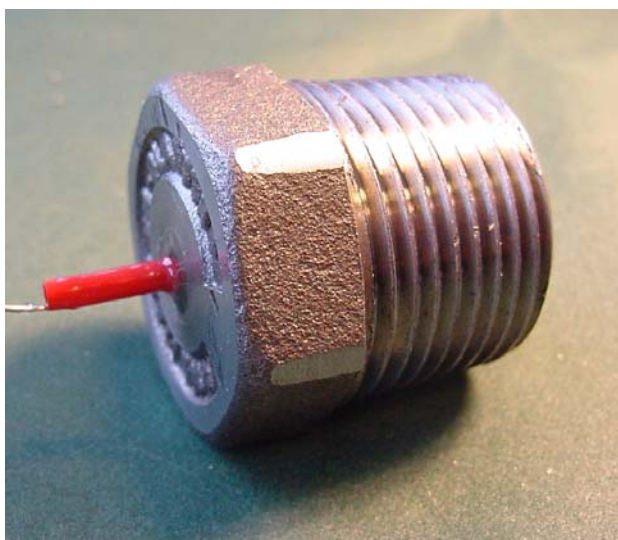


Fig. 4.2.27. LOCOR[®] cell for assessment of crevice corrosion. (Force Technology).



Fig. 4.2.28. ER probe. (MetriCorr).

With this equipment, the intensified test was completed with a total duration of 35 days (some 840 hours). There was no demand for heating at the plant throughout the entire period, and the water flow through the plant was quite modest – 25 m³/day. For comparison, the pump positioned in the by pass unit ensured that 175 m³/day process water was flowing through.

During the first 670 hours (~ 28 weeks) the plant was running without feeding make-up water. At this time, a provoked feeding with make-up water was commenced. Throughout a period of 21 hours, approximately 100 m³ make-up water was added, and as a consequence, the composition of the water passing through the by pass unit was almost identical to the composition of the pure make-up water.

The series of corrosion measurements performed throughout the period is illustrated schematically in Fig. 4.2.29. Environmental measurements (oxygen, pH, conductivity) were measured continuously throughout the period.

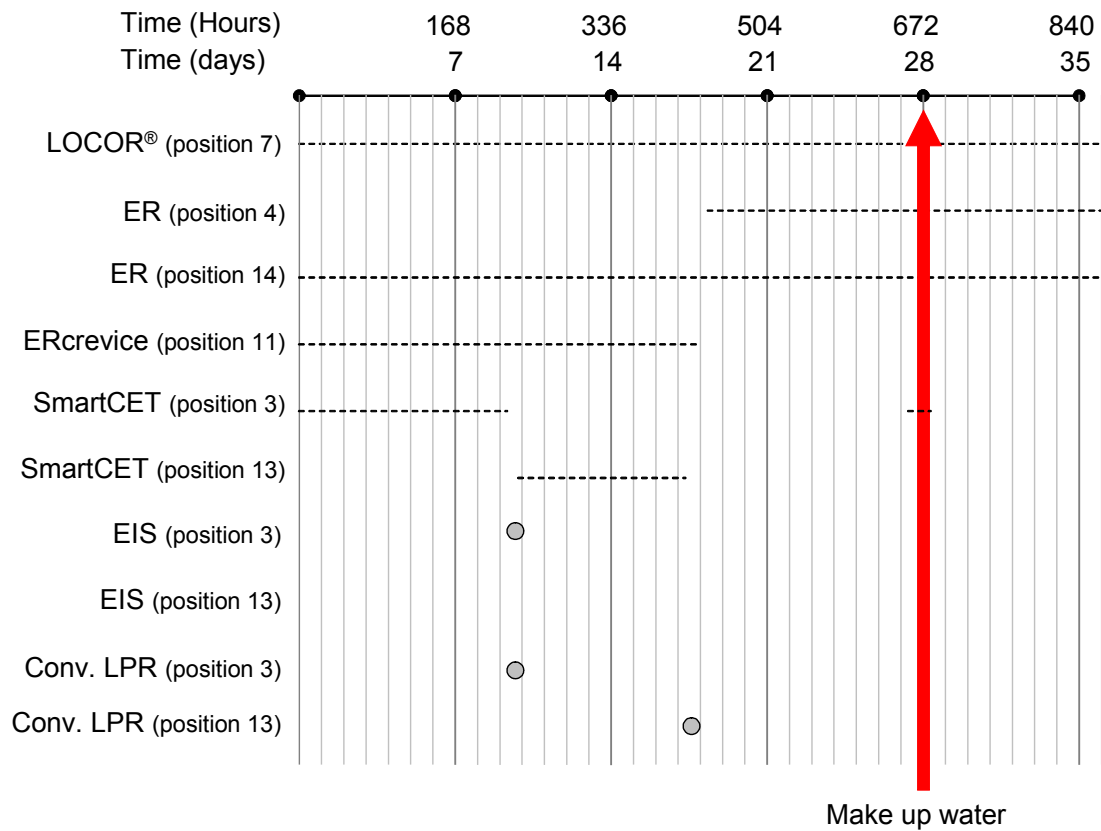


Fig. 4.2.29. Schematic presentation of activities at NB plant Odense.

Figs. 4.2.30-33 show temperature, conductivity, pH, and oxygen profiles throughout the test period. Obviously, the addition of make-up water influenced the environment heavily. Oxygen level was above datalogger range (max. 100 ppb) but readings on display on site showed above 500 ppb.

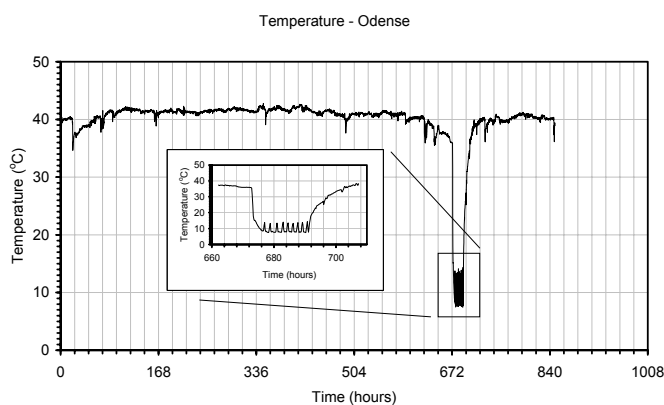


Fig. 4.2.30. Temperature profile.

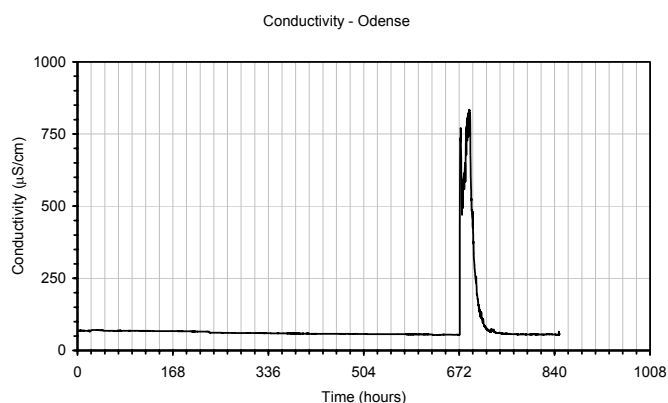


Fig. 4.2.31. Conductivity profile.

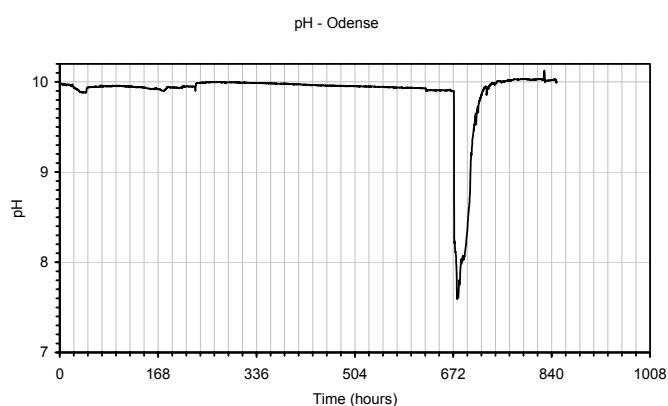


Fig. 4.2.32. pH profile.

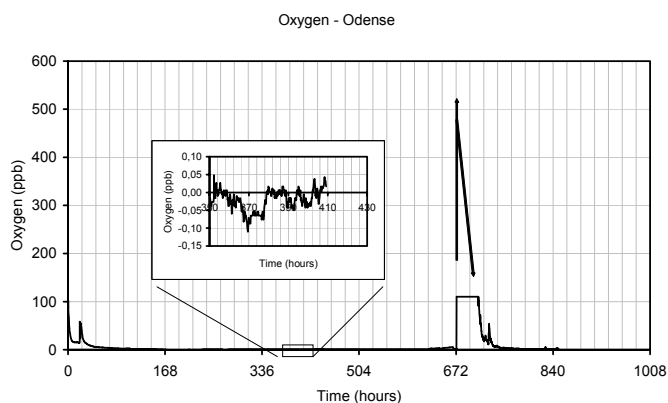
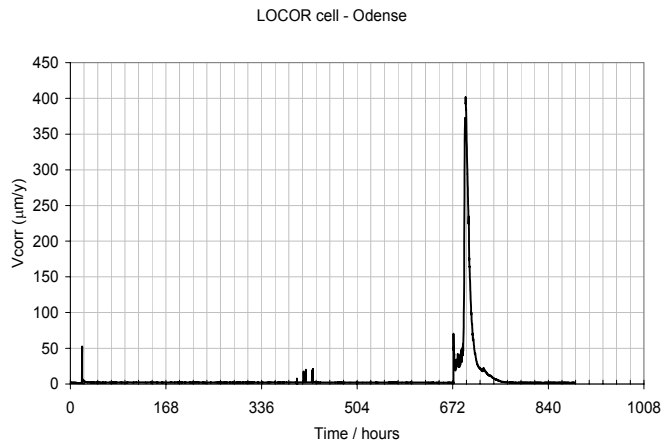


Fig. 4.2.33. Oxygen profile.

The results from the LOCOR[®] cell and the ER measurements are shown in Figs. 4.34-36. Both the LOCOR[®] principle and the ER measurements indicate zero corrosion in the steady state condition until addition of the make-up water. At this point, a distinct peak in corrosion rate occurs in both measurements in accordance with the peak in environmental parameters. ER detects 870 $\mu\text{m/y}$ while the LOCOR[®] cell (showing only the proportion of corrosion caused by establishment of a potential gradient across the internal glass frit) peaks at 400 $\mu\text{m/y}$.



**Fig. 4.2.34. Response LOCOR[®] cell.
(Corrosion rate calculated from
galvanic current).**

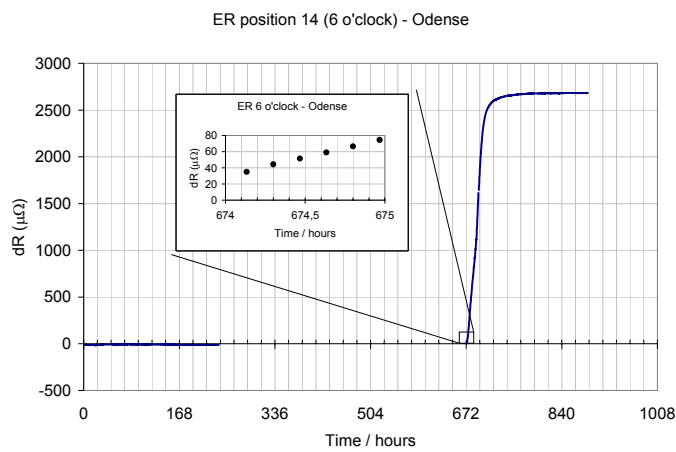
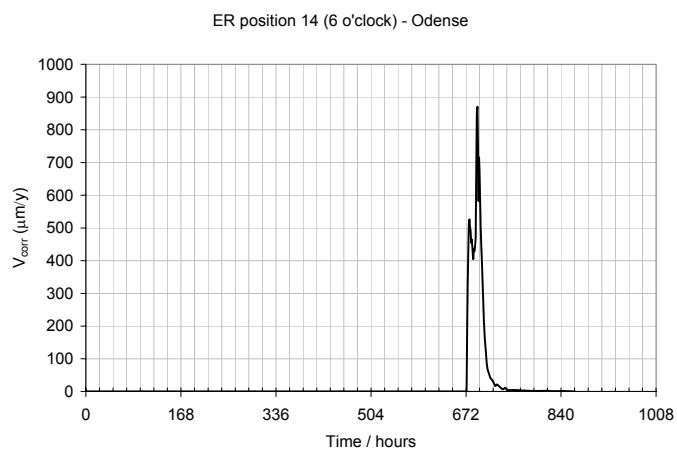


Fig. 4.2.35. ER response (raw data).



**Fig. 4.2.36. ER response (corrosion
rate).**

The SmartCET results are shown in Figs. 4.2.37-40 (12 o'clock position in which the equipment was positioned initially in the steady state period and during addition of make-up water) and Figs. 4.41-44 (6 o'clock position for a period with steady state condition).

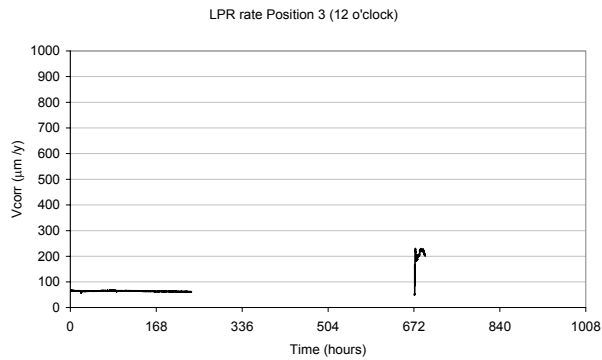


Fig. 4.2.37. SmartCET LPR Rate (12 o'clock).

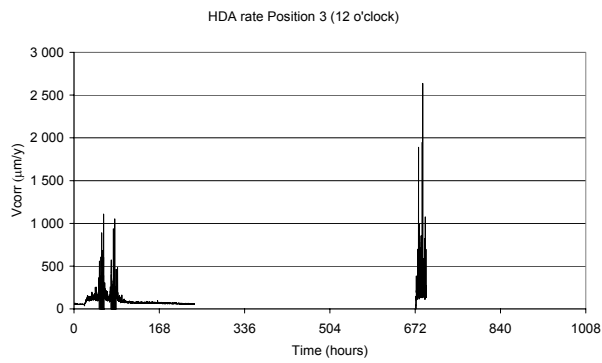


Fig. 4.2.38. SmartCET HDA Rate (12 o'clock).

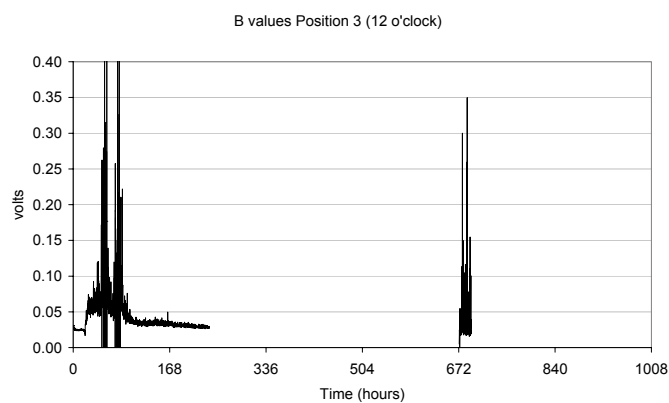


Fig. 4.2.39. SmartCET B-value (12 o'clock).

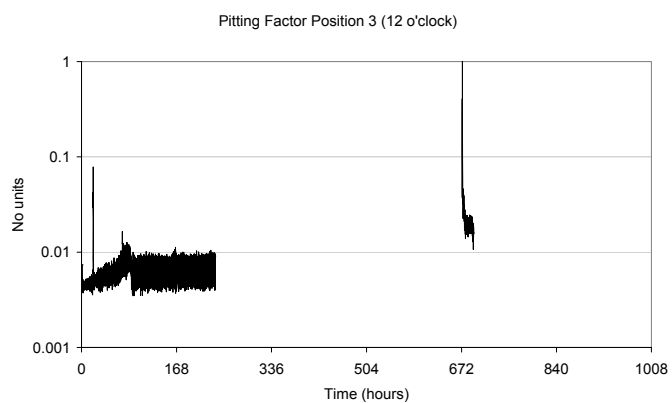


Fig. 4.2.40. SmartCET Pitting factor (12 o'clock).

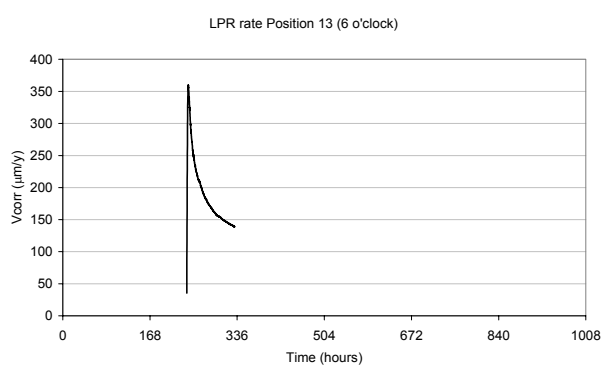


Fig. 4.2.41. SmartCET LPR Rate (6 o'clock).

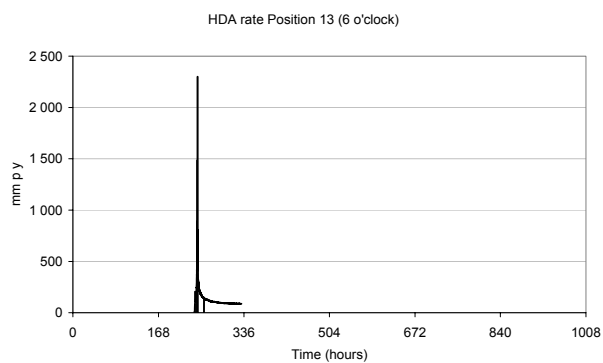


Fig. 4.2.42. SmartCET HDA Rate (6 o'clock).

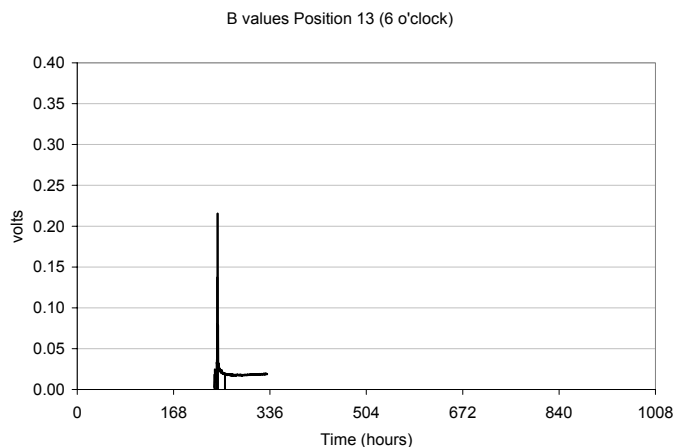


Fig. 4.2.43. SmartCET B-value (6 o'clock).

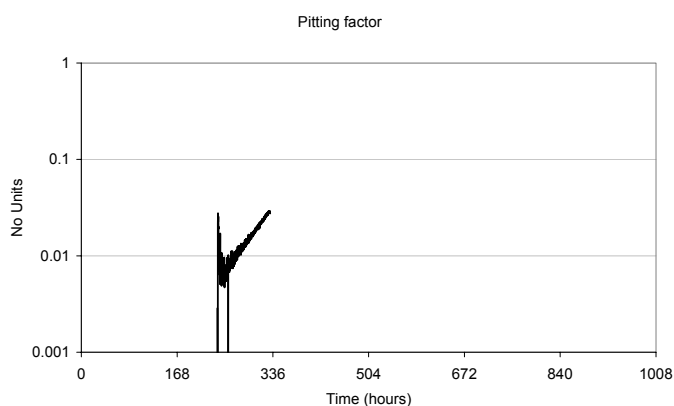


Fig. 4.2.44. SmartCET Pitting factor (6 o'clock).

From figs. 4.2.37-40 is observed that all the SmartCET measurements (LPR, HDA, B-value and pitting factor) detects the peak occurring during addition of the make-up water. During steady state condition, the system indicates corrosion rates below $100\mu\text{m/y}$ but significantly higher than indicated by ER and the LOCOR cell. SmartCET data from 6 o'clock position during steady state (figs. 4.2.41-44) also gave higher indications $100\text{-}300\mu\text{m/y}$. Conventional LPR and EIS gave values between 10 and $110\mu\text{m/y}$. Larger electrode area is mentioned as ideal for electrochemical measurements in low corrosivity water, just like ER elements are also designed and optimized according to equation 5.

Weight loss coupons were installed December 13th 2002 and withdrawn February 26th 2004 (i.e. exposed for 440 days). The measurements were invalidated since the plant operators by mistake shut off the circulation in the by pass unit, immediately after the intense measurements, thereby leaving the unit with no circulation and no fresh water additions for more than a year. With this in mind, the weight loss data (analyzed by Force Technology – also reported in sub-project 6) gave the results shown in table 4.2.3 – i.e. corrosion rates around $10\text{-}20\mu\text{m/yr}$.

The table however has little value, since as stated the valve to the by-pass containing the coupons was closed during most of the exposure. It is difficult to compare ER and SmartCET data with weight loss since there is no continuous monitoring data for the total exposure period.

The coupons exhibited both generally distributed corrosion as well as pits here and there (Fig. 4.2.45).

Table 4.2.3. Weight loss data.

Probe		initial g	Weight Final prior to cleansing g	Final after cleansing g	Weight loss		Vcorr $\mu\text{m/yr}$
					Corrosion products g	Total g	
5	12 o'clock	9,9667	9,9438	9,9314	0,0124	0,0353	9,8
6	12 o'clock	9,9519	9,9273	9,8988	0,0285	0,0531	14,7
10	6 o'clock	9,9865	9,9608	9,9192	0,0416	0,0673	18,7

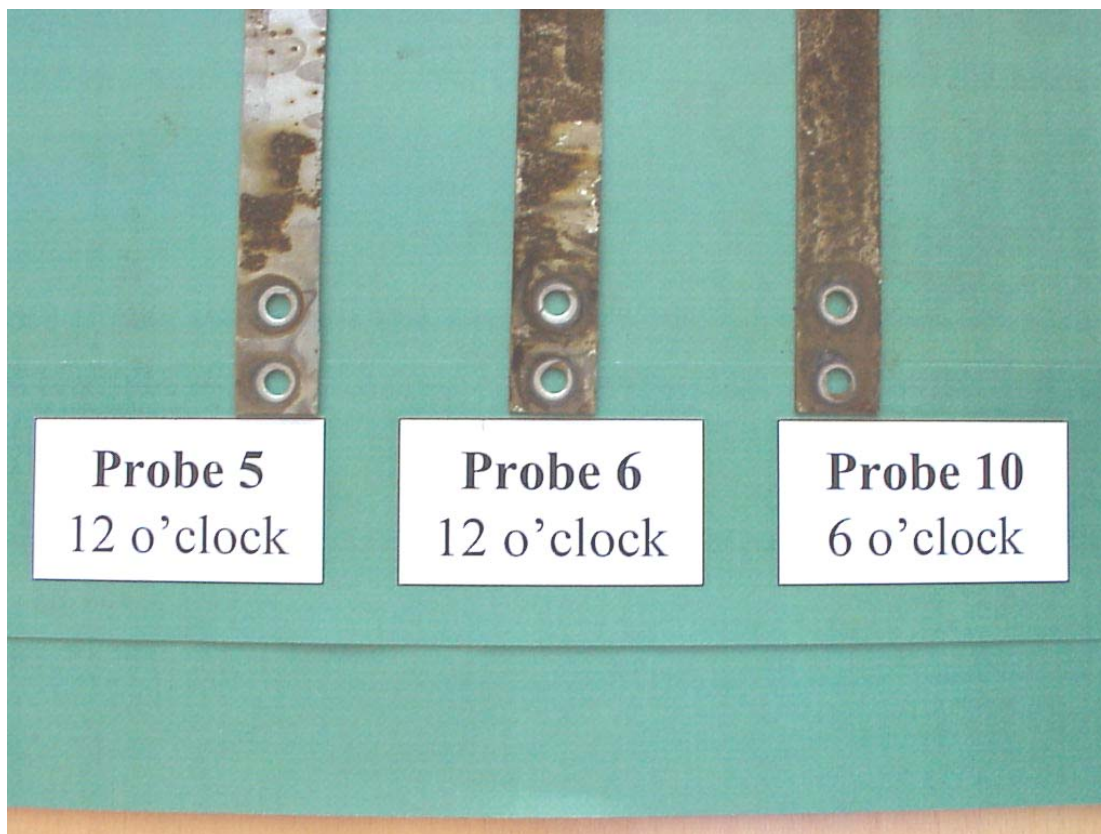


Fig. 4.2.45. Photo of the weight loss coupons after exposure.

Table 4.2.4 Environmental data and measured corrosion rates.

Parameter	Steady state	During water addition
Temperature (°C)	40	10
Conductivity (μS/cm)	50-60	800
pH	9.9	7.6
Oxygen (ppb)	0	500
V _{corr} – LOCOR (μm/y)	0	400
V _{corr} – ER 6 o'clock (μm/y)	0	870
V _{corr} - SmartCET LPR 12 o'clock (μm/y)	< 100 consistent*	200-250*
V _{corr} - SmartCET HDA 12 o'clock (μm/y)	< 100*	200-500*
V _{corr} - SmartCET LPR 6 o'clock (μm/y)	300-150*	-
V _{corr} - SmartCET HDA 6 o'clock (μm/y)	200-100*	-
V _{corr} – conv. LPR 12 – o'clock – 238 h (μm/y)	50	-
V _{corr} – EIS 12 o'clock – 238h (μm/y)	10	-
V _{corr} – conv. LPR 6 – o'clock – 238 h (μm/y)	110	-

For reference:

Hilbert, L.R., Thorarinsdottir, R. I., Andersen, A. and Nielsen, L.V, *Optimising corrosion monitoring in district heating systems*. ICC 2002 in Granada Spain September 22-27 2002.

Kane, R.D., *Online Real-Time Corrosion Monitoring of Hydrocarbon pipeline, plants and facilities – Development and experience*. ICC 2002 in Granada Spain September 22-27 2002.

J. A comparative field study performed in Iceland between the ER concept and the InterCorr SmartCET equipment.

Please refer to sub- project 3. ER data are shown in figs. 4.2.46 -47.

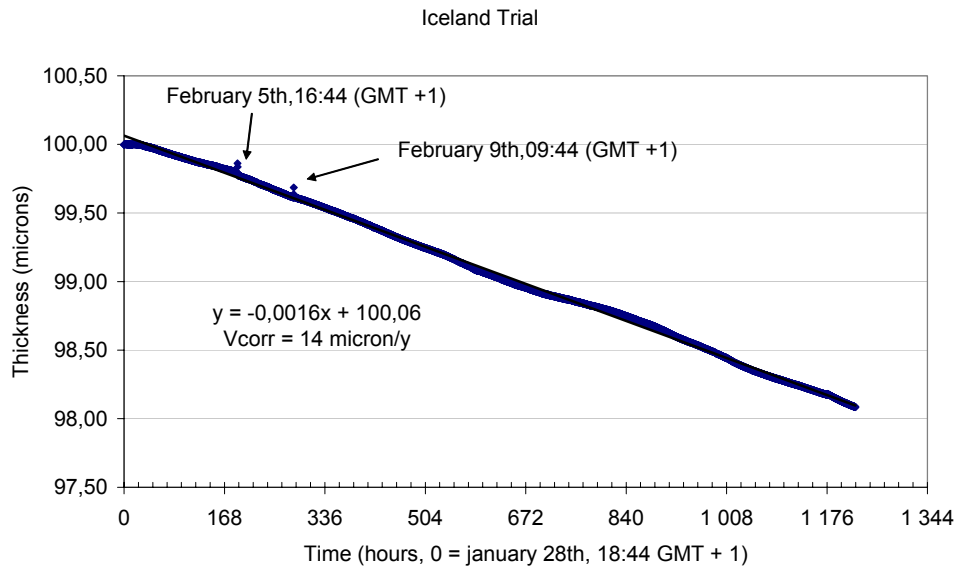


Fig. 4.2.46. Thickness on ER probe used in Iceland trial. General trend: corrosion rate 14 $\mu\text{m/y}$.

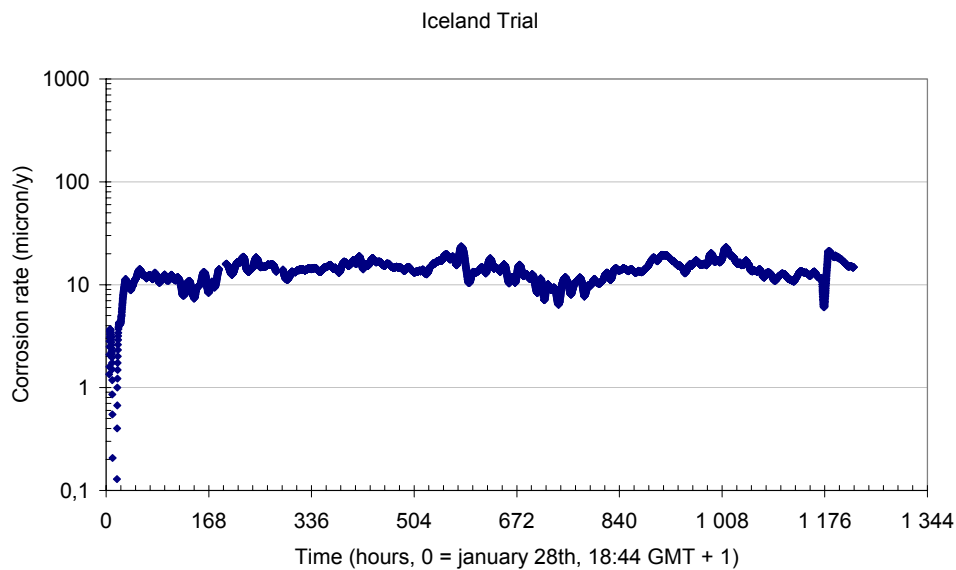


Fig. 4.2.47. Real-time corrosion rate measurement – Iceland trial.

Subproject 3 Comparative measurements on corrosion rate in district heating systems with different electrochemical techniques, ER and weight loss coupons

Responsible: Lisbeth R. Hilbert, DTU
Co-workers: Lars Vendelbo Nielsen, MetriCorr (former MetriCorr)
Kate Nielsen, FORCE Technology
Asbjørn Andersen, FORCE Technology
Ragnheidur I. Thorarinsdottir, IBRI
Magnus Nordling, KI
Olof Forsen, HUT
Participating district heating companies

Background

The primary objective of the project is to improve the quality control in district heating systems by corrosion monitoring. Subproject 3 focuses on reliability and applicability of monitoring techniques and includes work done by partners at DTU, MetriCorr, IBRI, HUT and KI.

In the majority of systems uniform corrosion is not considered a problem, but localized corrosion occurs – sometimes without any obvious connection with the water parameters monitored. The recommended Danish water quality includes a low conductivity, negligible oxygen content and pH values of approximately 9.8, which ideally leads to the formation of a protective layer of magnetite. Local breakdown of this passive layer followed by even a small ingress of oxygen may lead to severe localized corrosion. Thus, controlling pH and oxygen is important, but does not guarantee that corrosion is avoided. Corrosion monitoring techniques should therefore ideally monitor both general and localized corrosion reliably and fast. Furthermore, they must function well in the complex media found in district heating systems – including challenges like low conductivity, sulphide and biofilm.

In the specified Danish system water carbon steel will be expected to passivate under the formation of a stable magnetite film. Uniform corrosion rate is expected to be in the range of 2-3 $\mu\text{m yr}^{-1}$. Thermodynamic calculations with HSC Chemistry software for iron in 60°C pure water illustrated in an E-pH diagram (Fig. 4.3.1) show that magnetite Fe_3O_4 will be stable at low potentials in the pH area of 7 to 12. A decrease in pH can lead to loss of passivity, while a potential increase by e.g. oxygenation will be expected to lead to oxidation of magnetite and thereby formation of less protective hematite Fe_2O_3 . Magnetite deposits formed at high pH are typically dense and adherent, while magnetite formed at lower pH is less protective.

The passivity, however, implies a risk of localized corrosion. The anodic reaction can be localized on e.g. an area covered with deposits and oxygen ingress can cause a localized cathodic reaction on the passive surfaces, thereby forming an oxygen concentration cell. Increasing conductivity enhances the rate of localized corrosion as the range of the corrosion element is increased, so a larger area can act as cathode and crevices can be activated as anodes. With larger changes in the media causing severe loss of passivity as e.g. a strong pH decrease, the uniform corrosion rate can increase while the tendency to localized corrosion can be reduced, since the entire surface will be actively corroding.

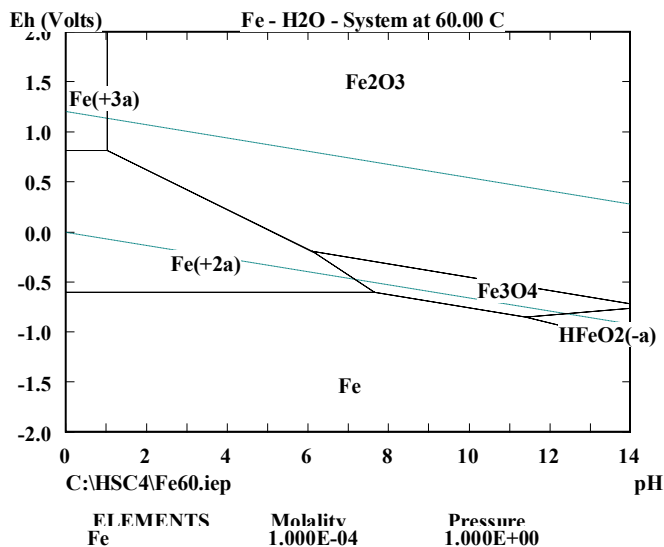


Fig. 4.3.1 Eh-pH diagram for iron in pure water at 60 °C, dissolved ions 1E-04 mol·l⁻¹.

In district heating systems in Iceland geothermal, sulphide-containing water is mainly used. Corrosion in these systems is normally small. The oxygen level is kept low, the conductivity of the water is relatively low and the pH value of the water is normally 9-10. The sulphide in the water is not found to result in high uniform corrosion rates in oxygen free water, but it seems that sulphur compounds in the water can cause local attacks. Sulphur appears in oxidation states ranging from – 2 to +6 and can play an important role in electrochemical processes. In oxygen free geothermal water the sulphur is mainly present as sulphide and sulphate. The sulphide causes a shift in equilibrium potentials of metals, which may result in severe local corrosion attacks. Furthermore, sulphide makes metals more vulnerable to even traces of oxygen and other reducible species, increasing the corrosion rate. Alloys rich in copper are especially susceptible to corrosion in such cases and selective attacks have been found in copper rich alloys in contact with more noble surfaces, e.g. in copper rich brazing metals¹⁶.

Oxygen entering a hydrogen sulphide containing environment may increase the corrosion rate by direct oxidation of the metal. Some of the oxygen will react with sulphide producing sulphate through intermediate compounds such as sulphite and thiosulphate. The product formation depends on the concentration of the reactants, the pH and temperature of the solution and the presence of metallic species. The intermediate compounds are found to be stable for long periods in the water. These compounds may result in local corrosion attacks as found in earlier research¹⁷.

This section will cover primarily activities at DTU followed by activities at IBRI. The activities at the five participating partners are focused on different techniques or systems, but all within the frame of evaluating applicability of techniques for a specific use. IBRI has focused activities on electrochemical techniques in sulphide media. MetriCorr has been actively involved in the ER technique, which is mostly reported in subproject 2. HUT has reported positive results with a galvanic probe for oxygen detection, and data is reported in subproject 4. KI is monitoring with weight loss and microbiological analyses for biocorrosion. The simple bypass unit designed at KI is mounted in district heating and cooling systems and coupons withdrawn periodically. The design is

¹⁶ R. I. Thorarinsdottir, Corrosion of copper and copper alloys in geothermal district heating water containing sulphide, Ph.D. thesis, Department of Manufacturing Engineering, The Technical University of Denmark (2000).

¹⁷ T. Hemmingsen, The effect of sulphite on corrosion, Ph.D. thesis, The University of Bergen (1992)

a pipe section with small pipes sections of carbon steel inside. These can be removed by opening the bypass pipe for a short while. There has been no real time on-line monitoring in the KI activities, which will be described in detail in subproject 5.

Results from subproject 6A are described in detail later in this report, but some data will be shown here for the discussion of the applicability of techniques in district heating systems.

Activities

2001

The initial studies in 2001 were focused on the use of electrochemical techniques in low conductivity media and studying the basic behaviour of carbon steel in anaerobic, alkaline media. The use of simplified simulated district heating water was used as a reproducible alternative to real district heating water. Different electrode holders were tested, but most of them lead to water ingress in the crevice between electrode and holder resulting in a strong effect on the EIS data. There was a tendency to occurrence of localized corrosion in the media. The low conductivity water gave a distinct effect on the high frequency EIS data, and the EIS data from deaerated and aerated conditions were very different. The IR drop was small due to the low currents and this resulted in the successful production of a polarisation curve in district heating water showing the stability of passivity films.

2002

Initial studies in 2002 were focussed on the crevice corrosion cell developed by FORCE technology. Focusing on measuring techniques, DTU studied and evaluated the validity of various electrochemical techniques for use in district heating systems. The use of high-sensitive electrical resistance (ER) probes developed by MetriCorr was also included in these studies. Electrochemical impedance spectroscopy (EIS), linear polarisation resistance (LPR), high-sensitive electrical resistance (ER) technology, crevice corrosion probes, as well as weight loss coupons were included in the evaluation. Laboratory studies in standard corrosion cells and in the prototype side-stream unit were included in the practical part of the project. Furthermore, monitoring was made in the first field unit in Ballerup.

Sonja Richter from IBRI visited DTU twice for experimental work and courses. In a few experiments conducted in hydrogen sulphide media EIS, LPR and ER was applied to test the sensitivity of the ER technique in comparison with the others. With this technique there was a promptly reaction to oxygen ingress and very high corrosion rates were measured indicating the potential risk of high corrosion rates in sulphide media.

Biocorrosion monitoring is covered by KI in subproject 5, however, for subproject 3 considerations were made on how to monitor biocorrosion. Two meetings took place with specialists from Danish Technological Institute with the purpose of choosing an appropriate way of monitoring. Based on the information gained at a biofilm monitoring conference there is no ideal on-line monitoring technique available for this type of system. During a visit at KI their way of handling the problem was discussed. No on-line monitoring is applied at KI, but analyses made on withdrawn coupons. It was decided that there will be no systematic biocorrosion monitoring in the Danish project,

however a few microbiological analyses will be made on selected weight loss coupons in order to get an indication of the presence of biofilm.

At Aalborg University microbially influenced corrosion in district heating water is being studied by a group lead by Professor Per Halkjær Nielsen. Lisbeth Hilbert visited this lab in October 2002. There were no plans in this group to apply neither on-line biofilm monitoring nor on-line corrosion monitoring. Corrosion was also here evaluated by weight loss and visual inspection of coupons. To ensure a minimum of correlation with the work performed in this project with the work at Aalborg University the same type of biofilm analyses will be applied – that is enumeration of cells (live and dead) by DAPI staining and FISH for identification of sulphate-reducing bacteria. The latter is more expensive and was not used in all sites.

Three Danish engineering students finished their bachelor project on corrosion monitoring in district heating resulting in two reports and three others were trainees at Force Technology and IBRI during autumn 2002.

2003

The first part of 2003 was focussed on field measurements (also part of project 6A), laboratory tests with commercial equipment from Intecorr (also project 2), and laboratory experiments on effect of sulphide (also project 1). The studies on effect of sulphide were a result of a 3 months stay of Tor Hemmingsen at DTU. The data from these experiments was presented in a paper at Eurocorr 2003 Budapest (Hemmingsen et al). Tor Hemmingsen made two presentations during his stay in Denmark – internally for the staff at IPL, DTU and one at a well attended meeting for members of the Danish Electrochemical Society. Lisbeth Hilbert made a short 2 day visit at Stavanger University in May 2003.

Test with Intecorr equipment was the positive result of communication with Dr. R. Kane. The equipment was delivered at DTU in the end of December 2002 and applied for tests in the laboratory, and at the Odense test site in January. Afterwards it was shipped to Iceland for further testing in geothermal systems.

In spring 2003 the results present at that time were evaluated in cooperation with other participants in the project and compared between different district heating companies and different countries. The student trainees concluded their reports, one paper and one conference paper. Trainee from IBRI Linda Nørskov presented her work at Eurocorr Budapest.

Field tests were made at Odense, VEKS (Karlslunde), Aalborg, Viborg and two units (heating and cooling systems) at Lundbeck pharmaceutical plant (data presented under project 6A). Results from laboratory and field tests with the crevice corrosion cell were presented in a paper at Eurocorr 2003 Budapest (Andersen et al.) and these data are also a part of project 6A.

Lisbeth Hilbert attended a one day biofilm seminar at Aalborg University with Professor Per Halkjær Nielsen. Arrangements were made for biofilm samples to be analysed at request. Discussions about mode of shipping samples were not concluded, but the activity awaited the precise time schedule from project 6A.

2004

A paper summarising the results of subproject 3 including thermodynamic calculations for corrosion in district heating water was presented at Dansk Metallurgisk Selskabs Vintermøde (Annual meeting of the Danish Metallurgical Society).

Laboratory experiments were conducted to investigate findings from the field test and the effect of heavy corrosion on performance of the probes. An evaluation of possible indications of microbially influenced corrosion risk was made by biofilm analysis of selected probes from all units. All weight loss coupons and probes were retrieved from units and final results gathered, analysed and discussed in the project group.

The final results was presented to the Danish District Heating Association and participating Danish district heating industry at a meeting on March 23rd 2004 as well as at the 13th Nordic Corrosion Conference in Iceland April 2004. Furthermore, the obtained knowledge on corrosion monitoring techniques was communicated to young Nordic researchers at a Ph.D. course financed by NORFA in Iceland, April 2004.

Results

The following section includes sections on Laboratory tests^{18,19}, Initial field tests²⁰, Comments on test of Intercorr equipment, Results from units in district heating^{21,22,23} (subproject 6A), Final laboratory tests, and Results from the Icelandic part of subproject 3. Laboratory results relating to sulphide media was described in subproject 1, and detailed discussion of Intercorr equipment test in subproject 2.

Laboratory tests

Experimental

In laboratory experiments simulated district heating water has been used under either oxygen purged or nitrogen purged conditions at room temperature or at elevated temperatures at maximum 65°C. The simulated district heating water is a very dilute borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) buffer solution (2.5E-05 M borax, 8E-05 M NaOH), which makes it possible to keep pH 9.8 and conductivity at 20-25 $\mu\text{S}/\text{cm}$. Laboratory experiments in the prototype unit (Fig. 4.3.2) have been conducted with recirculation of simulated district heating water at fully deaerated conditions (nitrogen purging), but also under controlled oxygen inlet. Media as given in Fig. 4.3.8 and 4.3.9 corresponds to pH 9.8: 0% air, 15% air, 40% air, and media in pH 8.3: 0% (deaeration), 5% air, 15% air, 40% air. Temperature was controlled at 60°C and the unit was run at low pressure of 1-2 bars.

¹⁸ M. Houlberg, Korrosion i fjernvarmeanlæg, M.Sc. thesis, DTU, Denmark, 2002

¹⁹ A. Højman, P. S. Lind, Korrosion i fjernvarmesystemer, M.Sc. thesis, DTU, Denmark, 2002

²⁰ R. Rubæk & K. Korsbæk, Praktikrapport om korrosionsmonitoring i fjernvarmesystemer, FORCE Technology & DTU, Denmark, 2003

²¹ L.R. Hilbert et al, Optimising corrosion monitoring in district heating systems, ICC 2002, Granada, Spain

²² L.R. Hilbert, Monitoring af korrosion i fjernvarmesystemer, Dansk Metallurgisk Selskab, Vintermødet, Kolding, Denmark, 2004

²³ L.R. Hilbert et al, Comparison of corrosion monitoring techniques in district heating systems, Nordic Corrosion Conference 13, Reykjavik, Iceland, 2004

Tests of electrochemical techniques

Electrochemical impedance spectroscopy (EIS) is a technique especially suitable for separating contributions from different electrochemical elements thereby enabling e.g. the separation of solution resistance and polarisation resistance. The operational conditions were amplitude 10 mV, frequency range 100 kHz to 0.1 mHz, 6 points pr decade. Data are fitted with Equivalent Circuit by B.A. Boukamp. Linear polarisation resistance (LPR) measurements are usually not suitable for low conductivity media since the high solution resistance will be added to the polarisation resistance and mask the response. However, this technique is faster and more widely applied for commercial monitoring than EIS. The operational conditions were scan rate 3 mV/minute and amplitude ± 10 mV.

Both EIS and LPR were carried out on a GAMRY FAS1. EIS and LPR have been applied in laboratory experiments in separate glass corrosion cells as well as in the prototype test unit. Glass cell experiments were carried out in a Faraday cage. Data will be given from standard glass working electrode holders or a three-electrode holder designed for the test unit. In the latter design all three electrodes are similar rod carbon steel electrodes of 9.4 cm² area each (Fig. 4.3.2). The carbon steel electrodes have been wet polished to grit 1000, rinsed in water and ethanol and dried in hot air before exposure. A platinum electrode was used as counter electrode in glass cell experiments and two similar carbon steel electrodes used for working and reference electrode in the unit experiments.

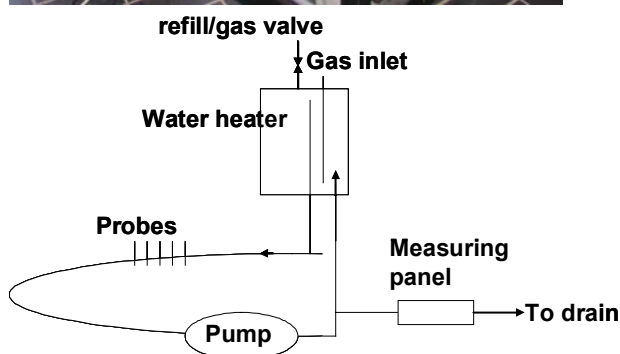


Fig. 4.3.2. *Right:* Prototype unit equipped with probes. The unit is connected to a gas purged water heater and *below* schematic of the lab unit setup.

***Left:* First prototype 3 electrode probe after 48 days exposure in lab unit.**

A crevice corrosion probe designed by FORCE Technology in an earlier Nordic Industrial Fund project²⁴ was also included. The cell is designed to favour the formation of local aggressive media under a glass frit. An iron disc of 1.77 cm² is the potential anode under the frit electrically isolated from the sides of the cell as well as the rest of the construction, which is the potential cathode. Current is measured between anode and cathode with a zero resistance ammeter and logged.

The modified high sensitive electrical resistance (ER) technique for corrosion rate measurement has been described in further detail in subproject 2. The principle was realised in instrumentation and probe (100 µm element thickness) especially designed for use in district heating systems. The probe was applied in the prototype test unit and corrosion rate was measured using the ER technology.

Results from electrochemical techniques

Fig. 4.3.3 is a typical EIS response obtained after 4 days exposure at 65°C in a glass cell. It appears that the response consists of a capacitive high frequency contribution, followed by a resistive feature in the range of 1000 Ω*cm², followed by two connected semicircles as seen in Nyquist presentation and possibly ending at low frequencies with a diffusion related part. The first part is analysed as an effect due to low conductivity, since it has been found that this high frequency feature disappears at higher conductivities (data not shown). It has also been found for a range of conductivities (20 to 1500 µS/cm) that the modulus of impedance at zero phase around 1000 Hz is inversely proportional to the conductivity and this value therefore represents the solution resistance R_s.

The two connected semicircles can be fitted for most measurements. The sum of resistances R₁ and R₂ is taken as the total polarisation resistance inversely proportional to corrosion rate. The low frequency diffusion effects cannot be analysed correctly unless more points are measured at lower frequencies. The time needed to obtain an EIS measurement is already 1½ to 2 days, and going to lower frequencies will increase this considerably. The slow response time is a combination of the low conductivity, the large polarisation resistances and the capacitances of maximum 800 µF/cm².

As a result the equivalent circuit in Fig. 4.3.3 can be applied for a simple analysis of data in the range of 1.5 kHz to 0.1 mHz. Solution resistance is 8.7 kΩ*cm², R₁ 5.3 kΩ*cm² and R₂ 2.1 MΩ*cm². In similar experiments at 25°C polarisation resistances of 0.26 to 1.4 MΩ*cm² are obtained. If a simple correlation of polarisation resistance to corrosion rate is applied assuming activation controlled reactions (B=26 mV), a corrosion rate of 0.15 µm/y can be estimated for the data in Fig. 4.3.3, while the data at 25°C give rates from 1.15 to 0.2 µm/y. With another electrode holder in glass cells corrosion rates were estimated 1-5 µm/y in N₂ purged media at 25°C with conductivity ranging from 25 to 1500 µS/cm. The lowest corrosion rate was found in the solution with the lowest conductivity. In oxygen purged media 7-15 µm/y were measured.

²⁴ M. Berggreen Petersen, P. Jansen, *Korrosion i fjernvarmesystemer*, Nordisk Industrifond projekt P 529 (1986)

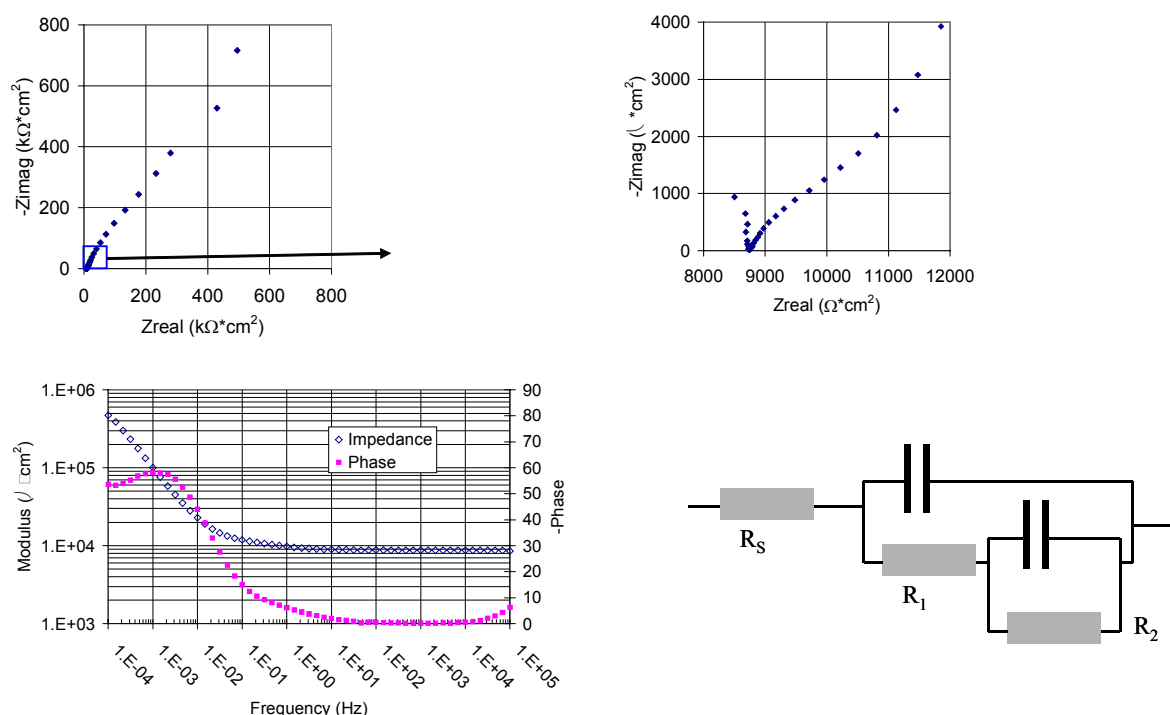


Fig. 4.3.3. EIS data from deaerated simulated district heating water, 4 days exposure, 65°C, as well as equivalent circuit applied for analysis of data from 1.5 kHz to 0.1 mHz.

Lab test unit

In the lab test unit polarisation resistances measured by EIS are in the range of 60-160 $\text{k}\Omega \cdot \text{cm}^2$ converted to corrosion rates in the range 4.8 to 1.8 $\mu\text{m}/\text{y}$. This is 5 to 10 times higher rates than measured in previous experiments. Due to high frequency noise in the unit, only data points from 400 Hz can be analysed. Curves are shown in Fig. 4.3.4 and results of analysis of two measurements in table 4.3.1.

Table 4.3.1. Resistances in $\Omega \cdot \text{cm}^2$, capacitances in F/cm^2 . Q and n refers to the capacitances.

Day	R_s	R_1	Q_1	N	R_2	Q_2	N
5	8080	16100	6.12E-04	0.65	(73000)	(2.5E-04)	(0.43)
24	8610	8200	5.57E-04	0.61	158000	8.58E-04	0.77

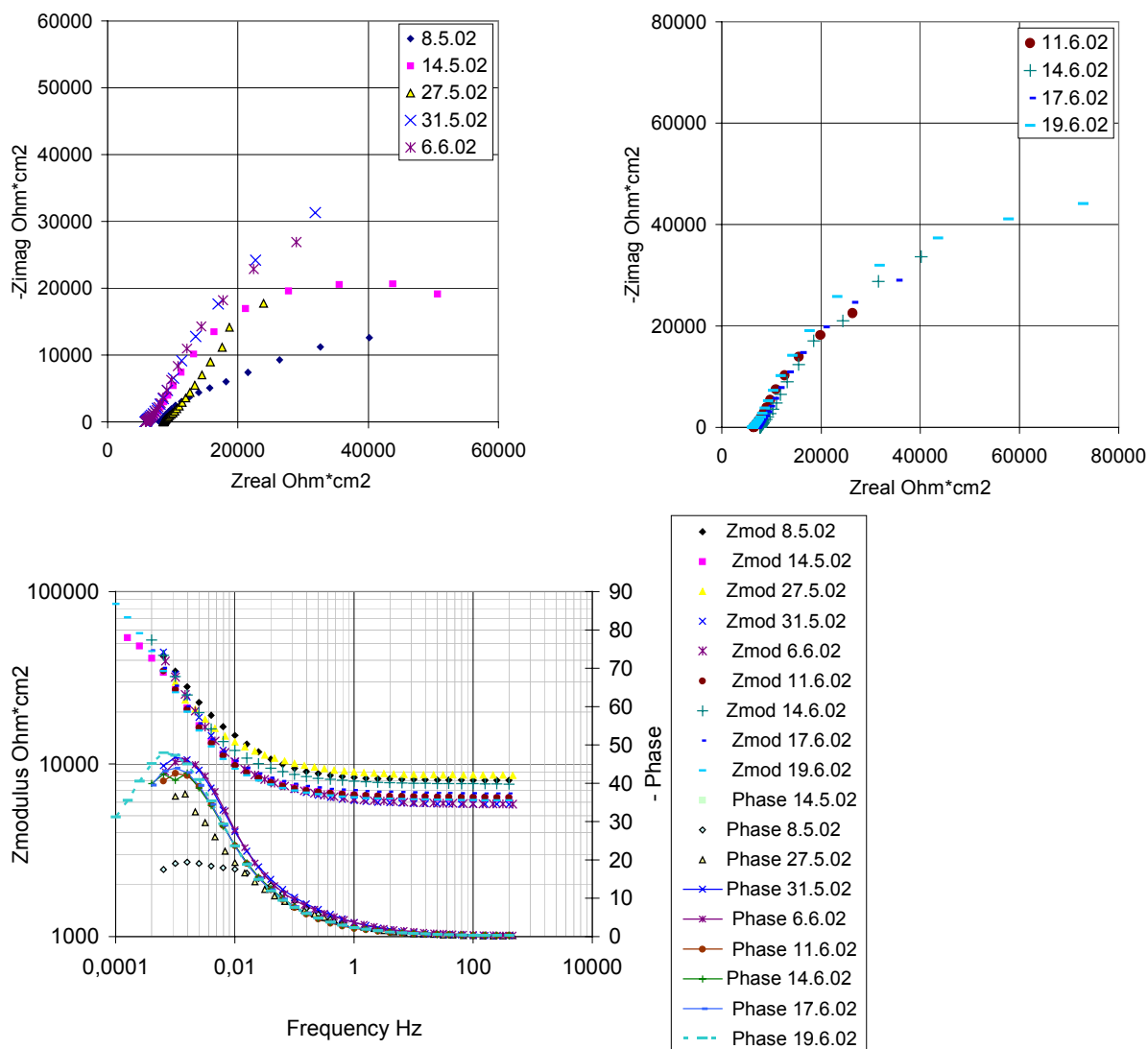


Fig. 4.3.4. EIS data from lab unit.

The LPR technique yields R_p values in the range of 18 to 70 $\text{k}\Omega \cdot \text{cm}^2$ in the unit. This is fairly lower than EIS. Solution resistance is dependent of the electrode design and in this setup 8 $\text{k}\Omega \cdot \text{cm}^2$ in 25 $\mu\text{S}/\text{cm}$ water can be measured. As long as corrosion rate is low and thereby R_p is high, the effect of R_s on LPR data will not be important, however at decreasing polarisation resistances, corrosion rate could be underestimated by LPR. IR compensation might be applied, but it is important to note that the R_s should be determined at fairly low frequencies (1000 Hz). Another effect leads to underestimation of the R_p from LPR. The scan rate is simply too fast to measure at a frequency, where zero phase is obtained, and thereby the total polarisation resistance. This is seen from the EIS data where zero phase is still not obtained at 0.1 mHz. Data at day 24 (May 27th shown in Fig. 4.3.5) is analysed to give 70 $\text{k}\Omega \cdot \text{cm}^2$ in comparison with the 160 $\text{k}\Omega \cdot \text{cm}^2$ measured by EIS on the same probe and on the same day. Furthermore, it is seen that the curve is only linear in a small range, which could make automatic data analysis invalid. The non-linearity can be seen on all measurements, but the degree of hysteresis can not be estimated, since the curves were only run anodically.

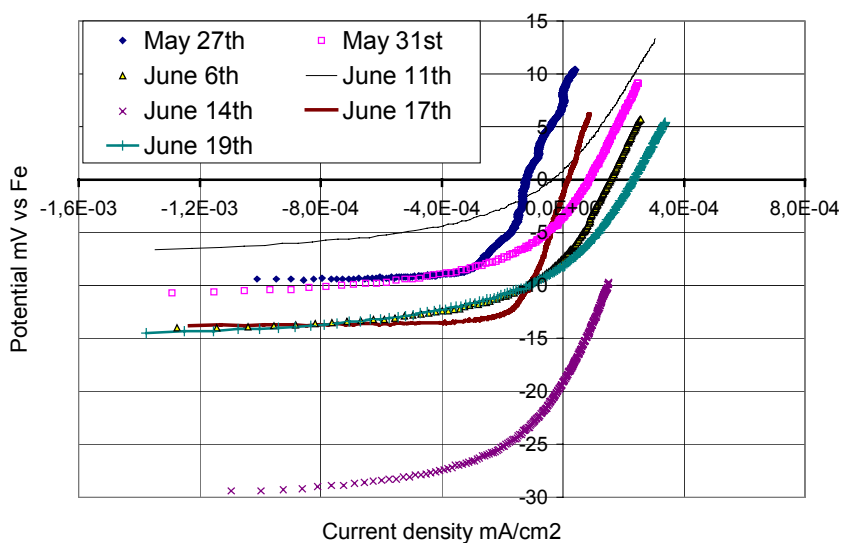


Fig. 4.3.5 LPR curves from lab unit all showing non-linearity.

High-sensitive electrical resistance

Fig. 4.3.6 shows response from the ER probe throughout a 1-hour test period in the unit during which the high-sensitive ER technique was actively recording the differential resistance. From the slopes of the curves the corrosion rate was calculated ($1.65 \mu\text{m/y}$). Fig. 4.3.7 shows the ER response after 250 hours giving a rate of $2.6 \mu\text{m/y}$. The ER corrosion rate of $1.65 \mu\text{m/y}$ from day 2 can be compared with the EIS response from day 5 (table 1) giving a corrosion rate of $3.3 \mu\text{m/y}$ with the corresponding LPR response giving $17 \mu\text{m/y}$. The values for ER and EIS are in the same range although the EIS indicates a 2 times higher rate. The measurement time is 12 minutes for LPR, 1 hour for ER and $1\frac{1}{2}$ days for EIS.

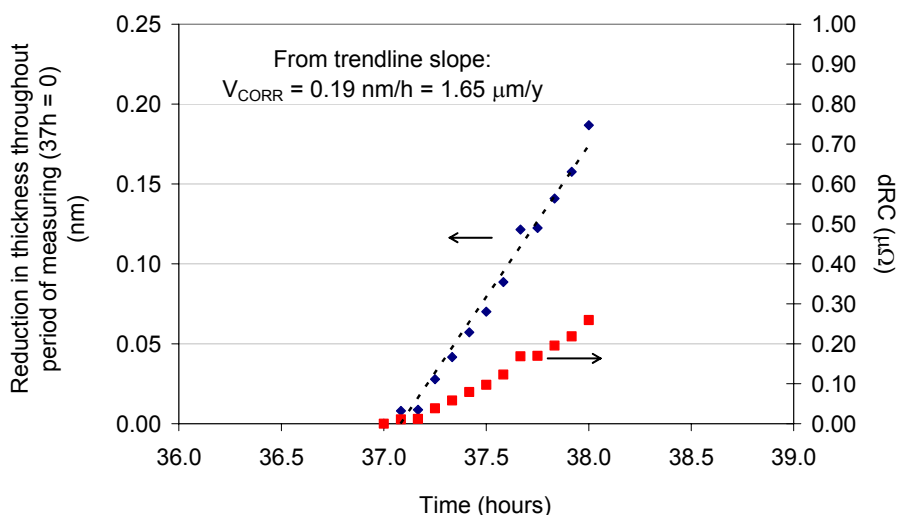


Fig. 4.3.6 ER-probe response in simulated district heating water after 37 hours of exposure.

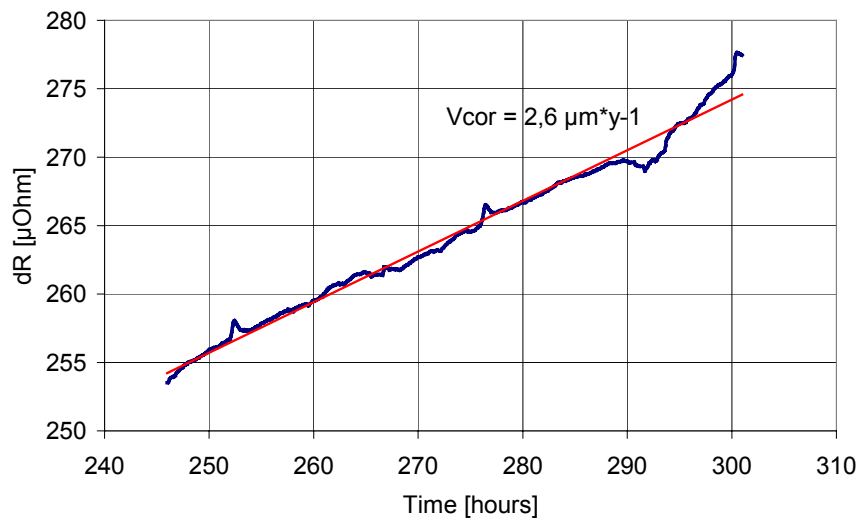


Fig. 4.3.7. ER response in lab unit after 250 hours exposure measuring 2.6 $\mu\text{m}/\text{y}$.

Fig. 4.3.6 illustrates measurement resolution of the ER technique. During the one-hour test period, the temperature compensated differential resistance increases by approximately $0.8 \mu\Omega$ with resolution below $0.1 \mu\Omega$. The corresponding reduction in thickness is 0.2 nm with resolution approximately 0.025 nm . The concept readily measures thickness reduction in the order of 0.5 ppm of the element thickness.

Crevice corrosion cell

The crevice corrosion probe responded to changes in oxygen content – but with a delay of 5 to 10 hours and with fairly low currents. No absolute value could be found correlating to a specific oxygen level, but there is a change in the current indicating the initiation of localized corrosion. This was not the case for the other techniques where no major change in corrosion rate was obtained.

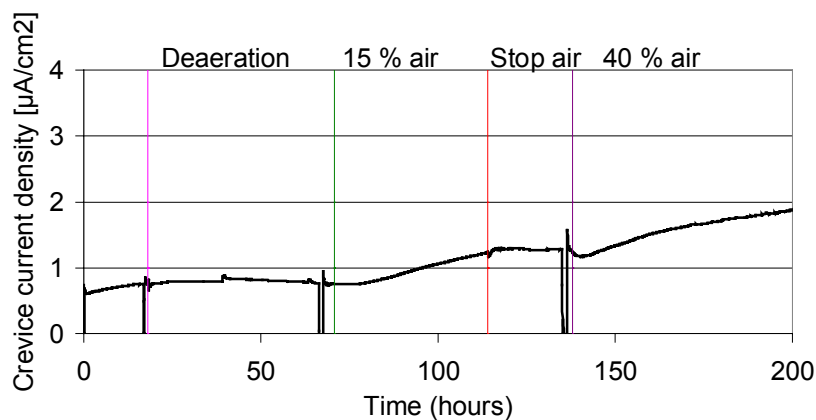


Fig. 4.3.8. Crevice corrosion cell coupling current, pH 9.8.

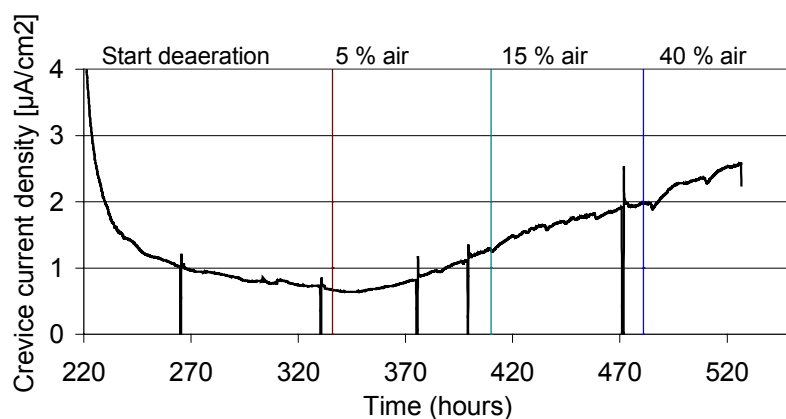


Fig. 4.3.9. Crevice corrosion cell coupling current, pH 8.3.

The range of corrosion rates measured by ER and EIS are within realistic values for this media and follow the same trends, however LPR fails to measure the very low rates. Data from the total 48 days experiment where the media was varied to provoke corrosion rate changes (Fig. 4.3.10) supports these findings. The media is either pH 9.8 or pH 8.3 and varying oxygen content.

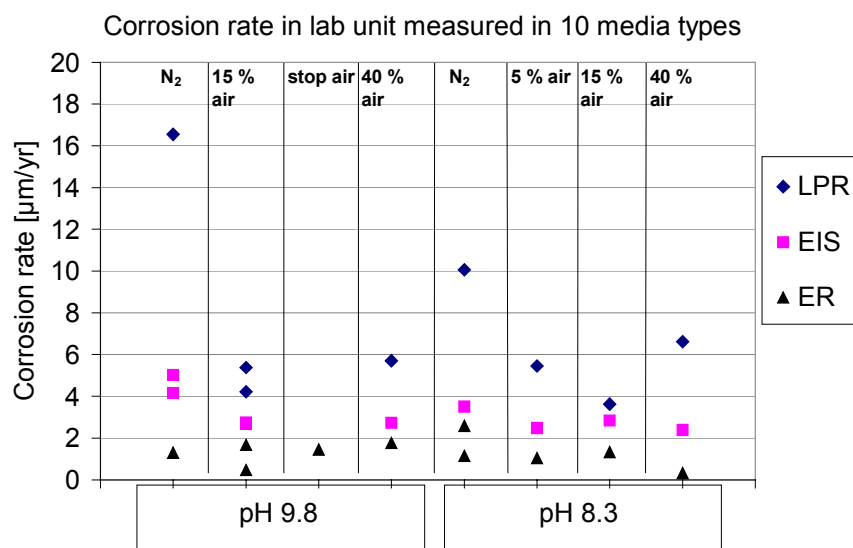


Fig. 4.3.10. Corrosion rates measured by ER, EIS and LPR in lab unit experiment.

It was expected that increased oxygen concentrations would also increase the general corrosion rate, but this was not the case. In low conductivity water with high pH the effect of oxygen is to facilitate formation of protective layers of magnetite or even haematite. If chlorides had been added to the system corrosion may have occurred, but in this buffered system only passivation took place. The

buffer is based on a very dilute borax solution. This may also have an inhibitory effect on corrosion, but 2.5×10^{-5} M is a very low concentration.

To support the thermodynamic considerations of corrosion the corrosion potential on carbon steel exposed in water from the E2 Energi-DTU plant (pH 9.7 and conductivity $34.8 \mu\text{Scm}^{-1}$) at 25°C has been measured to be -500 mV vs. SCE. A polarisation curve (Fig. 4.3.11) measured in this media with a low scan rate (0.05 mVs^{-1}) shows that the steel is passive and the corrosion rate is $0.8 \mu\text{A/cm}^2$ equal to app. $9.3 \mu\text{myr}^{-1}$ in the potential range of -510 to -370 mV vs. SCE. Exposure at this potential during a few days is expected to decrease the corrosion rate as a protective passive film builds up. IR compensation has not been included in the curve, since it appears that the IR drop only has an effect on currents above $10 \mu\text{Acm}^{-2}$, and data obtained at lower currents can thus be analysed directly. It is evident that LPR measurements performed on magnetite passivated surfaces could be difficult to interpret.

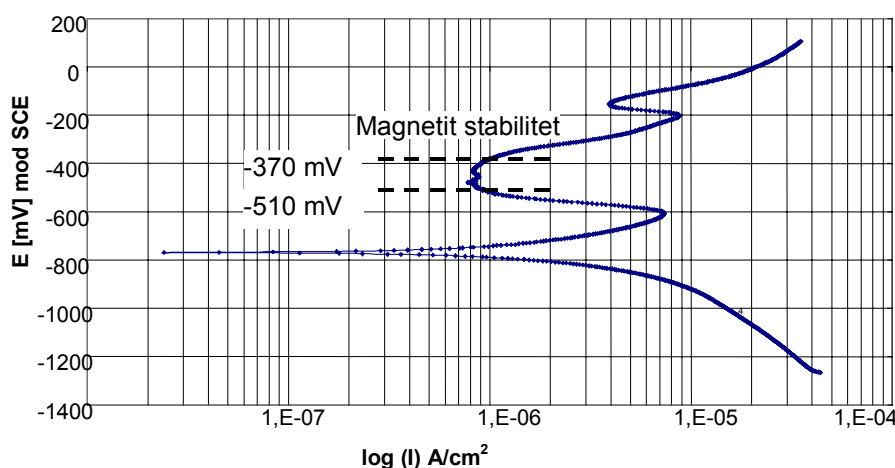


Fig. 4.3.11. Polarisation curve on carbon steel in district heating water from E2 Energi DTU.

Discussion of obtained data

A technique must function in the set-up, measure corrosion rate correctly and in reasonable time. So the purpose of the experiments was to compare the techniques in the same systems and analysing the potential errors of each technique. The fastest measurement is the LPR technique, however, there are strong indications that the requirements for applicability of LPR are not present and that data are more or less useless. Reasonably stable EIS measurements can be obtained even in the unit, however, high frequency data above 400 Hz are disturbed and low frequency data are very time-consuming to obtain. The requirement for a sensible measurement is that the system is stable during the two days period – meaning that sudden changes in corrosion rate or other electrochemical features will invalidate data. Furthermore, analysis is a function of the system and many pitfalls exist for wrong interpretation of data, e.g. ferrous sulphide deposits. However, for mechanistic studies of corrosion under stable conditions EIS could be a valid tool.

Based on the preliminary experiment we can conclude that EIS is too slow for real time monitoring, but does give valuable information on e.g. polarisation resistance. LPR is fast, but difficult to analyse and does not seem to give correct corrosion rates, whereas high-sensitive ER measures very low corrosion rates of e.g. 1.65 $\mu\text{m}/\text{y}$ in an hour. Localized corrosion does occur in the system as monitored by the crevice corrosion cell and it is a major drawback of all three methods, EIS, LPR and ER that they are only measuring general corrosion averaged on the entire surface.

Monitoring techniques have been applied in the prototype unit. The data support that the unit prototype is functioning as requested. However, LPR is found to be questionable for this system due to non linearity. For EIS both a simple and a more advanced analysis have been applied – leading to the observation that the simple analysis gives corrosion rates following the same trends as ER. Rates of 2 to 5 $\mu\text{m}/\text{yr}$ is found with EIS whereas ER gives very low rates of 0.3 to 3 $\mu\text{m}/\text{yr}$. There seems to be a correlation between EIS and ER, but EIS data give a factor 2 higher corrosion rate. Either the B value should be corrected or the ER iron foil corrodes more slowly than the steel rods used in the three electrode setup

The conclusion of lab unit experiments is:

- Initiation of localized corrosion might be found by the crevice cell
- 0.2-10 $\mu\text{m}/\text{yr}$ corrosion rates from lab data
- EIS does give stable measurements, but it takes two to three days
- Low conductivity does give a distinct contribution to EIS, but measurement is possible
- LPR measurements seem disturbed and generally show too high rates
- ER gives lower rates than EIS and LPR
- Passivation occurs at large oxygen ingress in simulated system water, which might be related to the borax buffer applied
- Both general corrosion and localized should be monitored

Initial field test

Results from Ballerup test site

The first prototype unit was installed at a central heating unit in Ballerup outside Copenhagen. Data of ER, crevice corrosion cell, EIS, LPR and chemical water analyses were recorded. Results of LPR and EIS measurements will be given in this section, the rest is given in subproject 6A.



Fig 4.3.12. Three electrode probe type used in Ballerup and all other field units.

The measurements were performed on a three electrode probe mounted in the top of the unit, and on one mounted in the bottom. The design of the probes had been slightly changed from the lab prototype. To reduce the risk of crevice corrosion between the single probes and the holders a groove was made in the probes to hold the o-ring between steel and Teflon and the separate probes were mounted closer.

An increase in R_s is observed over time, which could be related to film formation or change in conductivity. R_s is approximately 10 times lower than for similar probes in the lab unit – indicating that conductivity in Ballerup should be 10 times higher giving approximately 200-250 $\mu\text{S}/\text{cm}$. The actual measured values were 202 to 240 $\mu\text{S}/\text{cm}$.

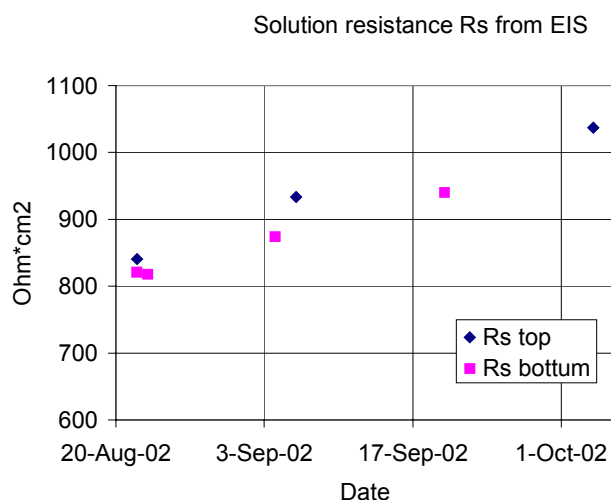


Fig. 4.3.13. Solution resistance obtained by EIS at Ballerup test site.

LPR measurements were as expected non-linear and dominated by hysteresis. Corrosion rates are expected to be low, meaning that the currents measured by LPR are also very small.

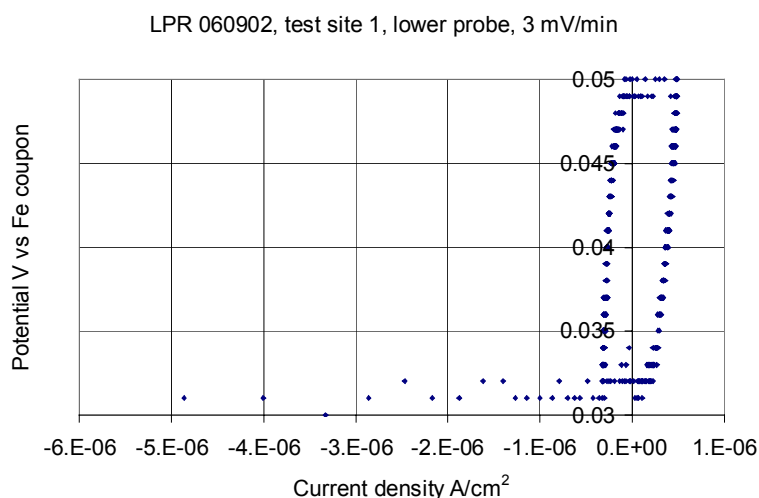


Fig. 4.3.14. Example of LPR measurement with a high degree of hysteresis.

The EIS data are large semicircles that are fairly simple to analyse, but since it takes 2-3 days to measure data points at low frequencies, the measurement time is very long. Corrosion rates calculated from EIS give less than 1 $\mu\text{m/y}$ corrosion rate, while LPR measurements give 5-10 times higher rates.

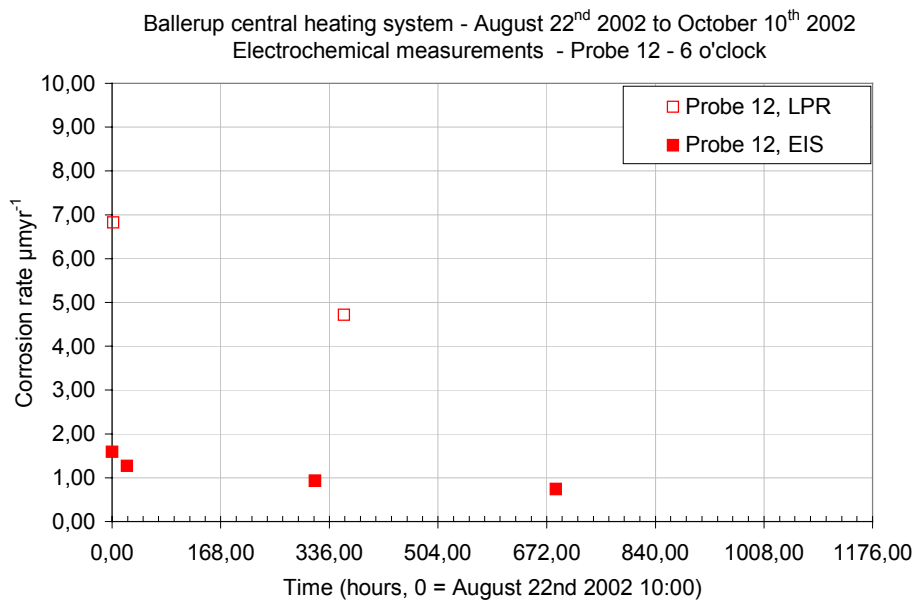


Fig. 4.3.15. Corrosion data obtained by EIS and LPR at Ballerup test site on 6 o'clock probe.

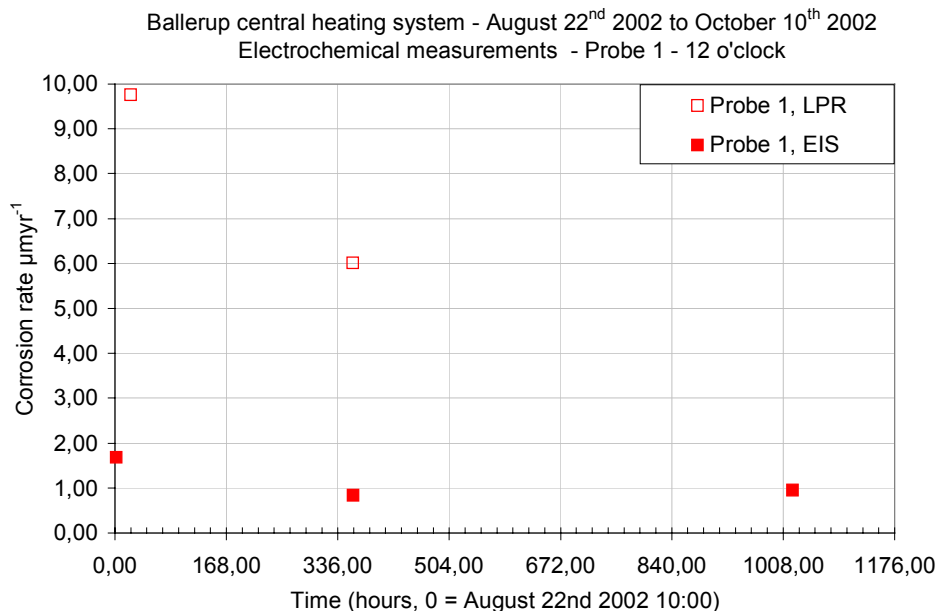


Fig. 4.3.16. Corrosion data obtained by EIS and LPR at Ballerup test site on 12 o'clock probe.

The crevice corrosion cell current measured is below 0.1 μA indicating negligible corrosion. However this may just be a good measure of the very non corrosive stable environment.

A single coupon from the system has been analysed for biofilm with fluorescence microscopy (DAPI) resulting in 5.2×10^4 cells/cm², which according to Professor Per Halkjær Nielsen, Aalborg University, is low compared to other district heating systems. This might relate to a fairly high operating temperature of 50°C or lack of nutrients. Weight loss after 5 months gave a result of 2.6 µm/yr.

In general the techniques were functioning well in Ballerup, but LPR data still seemed unreliable, and the crevice cell current seemed to generate very small current fluctuations affected by the large temperature variations in the room where the equipment was placed. Furthermore, ER data generated negative corrosion rates, which could not really be explained. Withdrawn ER probes were visually non-corroded, but whether conductive deposits may have affected the data is at this point not clear.

Comments on test of Intercorr equipment

As described in subproject 2 the equipment SmartCET[®] from Intercorr was tested. In this system LPR is used to determine corrosion rate, harmonic distortion analysis HDA is added to determine the correct B value for corrosion rate calculation, and electrochemical noise is applied to estimate the degree of localized corrosion. In this equipment for LPR an amplitude of 50 mV and a scan rate equivalent to approximately 1 mVs⁻¹ are applied and each measurement is therefore completed in a few minutes. Data is to be collected from continuous monitoring of longer time periods (hours/days) before analysis. Application of these techniques in low conductivity water is expected to be difficult, but for the district heating systems non-destructive, on-line, real time techniques would be perfect, and it is worth while testing whether any of these function well in the media.

An evaluation of the Intercorr equipment as compared to ER was given in subproject 2. Comparison with the LPR and EIS in laboratory test and field test at Odense shows that the results of Intercorr LPR and the LPR measurements of this project correlate. In the laboratory tests ER and Intercorr equipment also give comparable results. However, the application of electrochemical techniques in Odense gives overestimation both with Gamry equipment and Intercorr, and only ER gives a realistic value for the low corrosion rates. The feature of applying electrochemical noise for localized corrosion is very interesting and in the tests the pitting index did react to changes in the media both in lab and Odense. However, there were also examples of non explained high pitting indexes. The often change between monitoring technique in the tests may have given the Intercorr technique an unrealistic hard test. In conclusion the Intercorr equipment gives continuous monitoring of corrosion rate and risk of pitting, but the reliability is low in district heating water. Other experiences from Intercorr show that larger surface area of the probes improves the reliability when measuring low corrosion rates. From this subproject also the use of lower scan rates has been pointed out as very necessary for reliable LPR measurements. The instrument settings could therefore be optimised to the actual system, but it still seems that electrochemical techniques are too difficult to apply in these water types.

Results from units in district heating

Bypass units have been mounted on 7 Danish district heating plants. The unit is permanently mounted on the system, while the monitoring is conducted with a range of instruments shifted from one location to another. Values of corrosion rates and water chemistry parameters have been measured simultaneously for minimum 3 weeks at each system. The unit is described in subproject 6 and resulting data are all given in the plant reports in subproject 6A. This section will focus on the applicability of the techniques based on these results.

Background

Electrochemical techniques (linear polarisation resistance measurement LPR, electrochemical impedance spectroscopy EIS) as well as direct techniques (high-sensitive electrical resistance ER, crevice corrosion current, weight loss) have been applied. Crevice corrosion current measurement is an electrochemical technique, but since it directly measures the crevice corrosion current, it is here designated a direct technique. The techniques primarily measure uniform corrosion rates except for the crevice corrosion cell. LPR and EIS have only been applied periodically, but can be automated. High-sensitive ER and the crevice corrosion cell produce continuous data, while weight loss is based on periodical removal of separate probes.

With weight loss coupons accumulated corrosion is measured, and an average corrosion rate can be determined for e.g. a specific time period. The sensitivity of weight loss is low, which is why the recorded weight losses refer to an extended time period (6-12 months) as compared to the other techniques. This introduces an error when comparing the data, since the corrosion rate and the media might have changed during that time period. The benefit of weight loss coupons is that it is an extremely simple technique which includes the option to visually evaluate the type of corrosion and deposits.

Application of LPR and EIS in low conductivity water is expected to be difficult, but for the district heating systems non-destructive, on-line, real time techniques would be ideal, and it is therefore worthwhile testing them. The combined resistance measured with LPR is the sum of the solution resistance and the corrosion resistance. In case the solution resistance is high the error will be large and the corrosion rate underestimated. Laboratory tests in the project have, however, shown that the solution resistance R_s even in water with a conductivity as low as $25 \mu\text{Scm}^{-1}$ is less than 1/10 of the polarisation resistance R_p , indicating that the error will be acceptable for very low corrosion rates where R_p is large. Another aspect is that the scan rate must be adjusted to the time constant of the corrosion cell and e.g. in cells with large capacitive or diffusion effects very low scan rates must be applied²⁵. According to laboratory tests a scan rate of 0.005 mVs^{-1} will be applicable in district heating water. The Icelandic project partners have achieved reliable measurements in geothermal water with this scan rate^{26,27}, which is at least 10 times lower than the usual applied scan rates.

With EIS the contribution from solution resistance can be separated from the reactions of the corroding system. The drawback is that the corroding system may be slowly reacting so that an EIS

²⁵ L.R. Hilbert, Monitoring techniques for microbially influenced corrosion of carbon steel, Dansk Metallurgisk Selskab, Vintermødet, Sorø, Denmark, 2000

²⁶ L. Nørskov, Comparative studies of the reliability of electrochemical techniques in geothermal water, Engineering training report, IBRI, Iceland & DTU, Denmark, 2003

²⁷ Nørskov et al; Comparative studies of electrochemical methods in sulphide containing water distribution systems, EUROCORR' 2003, Budapest, Hungary

measurement will take days, and for an on-line, real time measurement this is unacceptable. Laboratory data shows that reliable measurements in this media may take up to 3 days.

A probe with three identical steel electrodes, each with an area of 9.4 cm^2 , is used for LPR and EIS. Measurements are conducted with a Gamry FAS 1. EIS measurements include 5 points pr. decade, amplitude of 10 mV and a frequency range of 100 kHz to minimum 100 μHz . LPR measurements are conducted either with 10 mV amplitude with 0.05 mVs^{-1} scan rate or with 5 mV amplitude and 0.005 mVs^{-1} scan rate. An empirical B value determined from laboratory and the initial field test in this project is 15 mV for steel in district heating water, but in treatment of data the theoretical value of 26 mV has been applied.

The high-sensitive electrical resistance method from MetriCorr is based on measuring electrical resistance changes caused by thickness reduction of a probe. With traditional ER technique the change in absolute resistance is taken as a measure of the accumulated corrosion rate over a longer time period – equivalent to a weight loss measurement. The benefit of the high-sensitive technique is that even small changes in resistance (in $\mu\Omega\text{hr}^{-1}$) can be determined accurately within a short time. Thereby it is possible to measure corrosion rates of $1 \mu\text{myr}^{-1}$ in a few hours^{28,29}.

The LOCOR cell is a probe designed to measure crevice corrosion^{30,31}. The central part of the probe is an iron electrode, which is electrically isolated from the rest of the system and which is mounted under a glass filter, which allows a certain transport of ions but still limits the diffusion. The galvanic current measured between the iron electrode and the rest of the system with a zero resistance ammeter (ZRA) is thus a measure of the crevice corrosion current on the iron electrode. No or low current indicates a low driving force for crevice corrosion while an increasing current indicates localized corrosion.

Performance of techniques

Weight loss data from all units give corrosion rates in the range of 2 to $19 \mu\text{m/y}$ dependent of the system. Localized corrosion, deposit formation or general corrosion can be visually identified on the coupons. In most units operational parameters for the unit was changed during the exposure time of the weight loss coupons, which makes the comparison with data from the 3 week intensive monitoring difficult. However, the obtained corrosion rate values seem reasonable and reliable for the systems in question, and data are included in the evaluation. An example is given in Fig. 4.3.17 and 4.3.18 of general vs. localized corrosion on probes with low averaged corrosion rates.

²⁸ L.V. Nielsen et al, Anvendelse af ER-målingen til karakterisering af metallers korrosionstilstand og øjeblikkelige korrosionshastighed, DMS Vintermøde 2002

²⁹ L.V. Nielsen, K.V. Nielsen, Differential ER-technology for measuring degree of accumulated corrosion as well as instant corrosion rate, NACE CORROSION '2003, Paper No. 03443, 2003

³⁰ A. Andersen et al, A localized corrosion cell for industrial applications, EUROCORR' 2003, Budapest, Hungary

³¹ A. Andersen et al, Development of a unit suitable for corrosion monitoring in district heating systems. Experiences with the LOCOR-cell* test method, Nordic Corrosion Conference 13, 2004, Reykjavik, Iceland

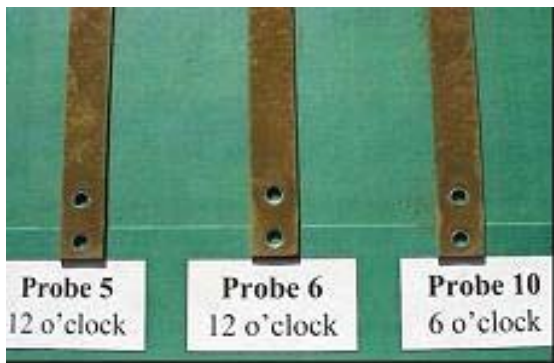


Fig. 4.3.17. Aalborg, 2 $\mu\text{m}/\text{yr}$, general corrosion and deposits **Fig. 4.3.18. Viborg, 3 $\mu\text{m}/\text{y}$, localized attacks**

The ER technique measured very low corrosion rates in most systems. The data were fairly stable and within hours very low rates could be determined. As an example the data from Aalborg are given in Fig. 4.3.19, where the thickness of the probe as a function of time is depicted.

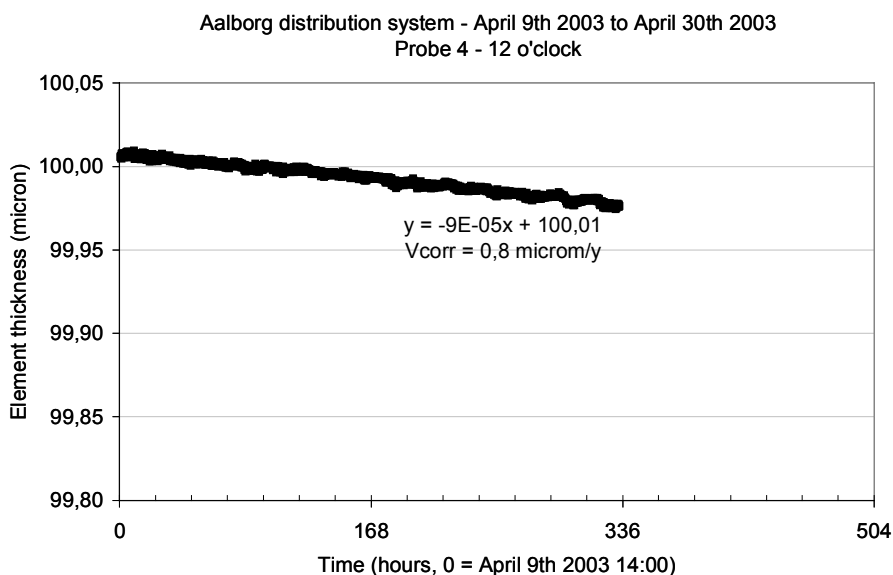


Fig. 4.3.19. Thickness reduction of ER probe 4 in Aalborg unit. Corrosion rate stable on 0.8 $\mu\text{m}/\text{yr}$.

The ER technique functioned in all the tested systems and a good response to changing media was found. Visual examination revealed primarily general corrosion on the probes, but e.g. on probes with an artificial deposit, localized attacks could be found just at the borderline between bare surface and covered surface.

Data from Odense is shown to illustrate the performance of ER and LOCOR cell in media going from non corrosive to very corrosive due to poor make-up water quality. On day 1 a planned boiler test was made, which is seen as an increased oxygen level in Fig. 4.3.20. In the following period the corrosion rate measured by ER was around $1 \mu\text{m}\text{yr}^{-1}$ and the crevice corrosion current negligible. Electrochemical measurements indicated larger rates of approximately 10 (EIS) to 100 (LPR) $\mu\text{m}\text{yr}^{-1}$ and clearly overestimated the corrosion rate.

After 28 days make-up water was supplied for 21 hours duration. The supply of make-up water was so large, that it can be assumed that the unit was almost entirely filled with make-up water as long as the addition of make-up water went on from 672 to 693 hours.

The environmental change is clearly seen on the increasing oxygen concentration, decreasing pH, increasing conductivity and decreasing temperature both during the actual make-up water addition and for approximately a day after. The environmental change furthermore results in a clear change in the corrosion rate measured by ER and by the crevice corrosion cell. These severe environmental changes lead to corrosion rates of up to $800 \mu\text{m}/\text{yr}$ (ER) and crevice currents up to $40 \mu\text{A}$.

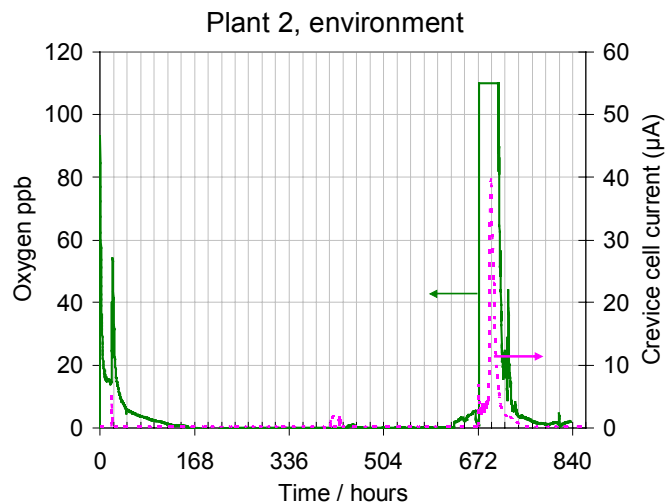


Fig. 4.3.20. Oxygen and crevice corrosion current – Odense

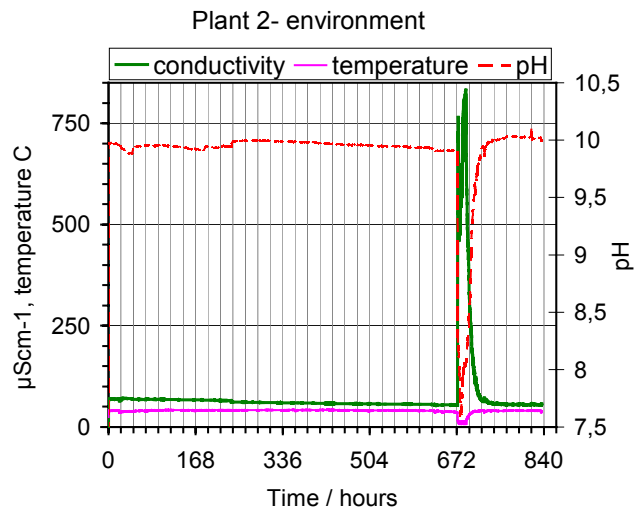


Fig. 4.3.21. Environment Odense.

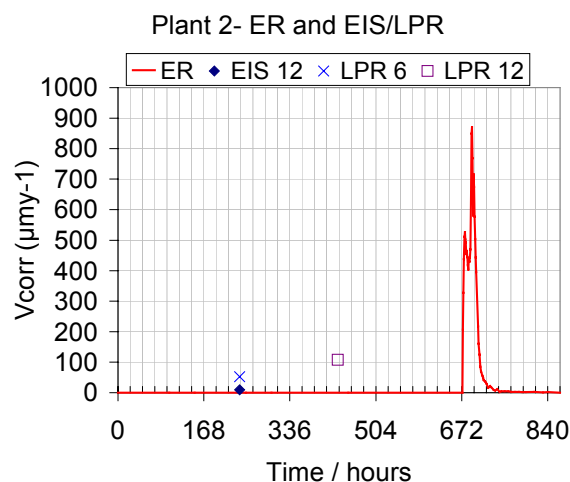


Fig. 4.3.22. Corrosion rate by ER, LPR/ EIS – Odense

In all systems except Odense, Viborg, and Lundbeck Central Heating the LOCOR cell gave currents close to 0 μA indicating no localized corrosion. In all systems with low current response from the LOCOR cell corrosion was uniform on the weight loss probes. The response in Odense was strong, but the conditions were very corrosive and severe corrosion attacks were found on weight loss probes. The attacks had initiated as localized attacks but spread to more general corrosion. However, bright non corroded areas could still be found on the probe surfaces after one year exposure. In Viborg the media was non corrosive but the LOCOR cell reacted to periodic small short term (max. 5 hours) oxygen levels of 100 ppb with current peaks of less than 1 μA . Indeed in this system pitting was found to have initiated on the weight loss probes. In Lundbeck central heating large amounts of make-up water generated a current response initially, but when the system was left undisturbed low currents were again measured. When examined after 6 months exposure corrosion attacks were, however, quite severe and no localisation could be identified.

Continuous electrochemical measurements with Intecorr equipment was also applied in Odense and did respond with an increase in corrosion rate during make-up water addition. But again the values for normal operation was overestimated and in the range of 100 $\mu\text{m}/\text{yr}$. Weight loss averaged over 440 days gave corrosion rates in the range of 10 to 19 $\mu\text{m}/\text{yr}$. Based on these data EIS and LPR clearly overestimated the rate during normal operation in Odense, while ER and LOCOR cell gave promising fast results.

In Ballerup and Odense only the high scan rate of 0.05 mV/s was used for LPR and these data overestimated the corrosion rate. A 10 times lower scan rate of 0.005 mV/s in the LPR measurements ("slow LPR") was applied together with the faster one in VEKS and Viborg. It was found that in VEKS the slow LPR also overestimated the rate, while in Viborg a more realistic value was obtained with the slow LPR ($< 2 \mu\text{m}/\text{yr}$). In Aalborg and the two Lundbeck units only slow LPR was applied and in Aalborg the slow LPR still overestimated the corrosion rate while the data from Lundbeck seemed more reliable.

With Viborg as an example, if the LPR measurements are conducted with a 10 times larger scan rate, the resistance values measured gives a corrosion rate in the range of 4 to 6 times larger than the slow LPR. The curves are not linear at any of the rates. In Fig. 4.3.23 LPR data obtained with both slow and normal scan rate on the 12 o'clock probe are shown. Neither of the curves is linear and hysteresis is dominating the response. Almost any slope can be fitted to these data. For this analysis a straight line has been fitted to the last part of the curve going from cathodic to anodic direction.

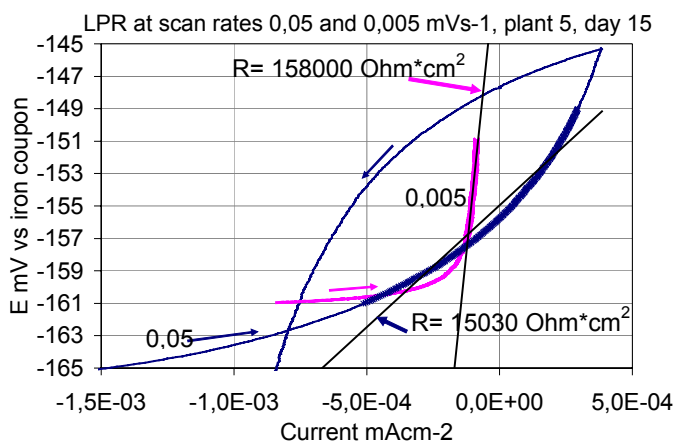


Fig. 4.3.23. LPR at two scan rates on probe 12 o'clock, day 15, Viborg.

Looking on the corresponding type of EIS in Fig. 4.3.24 it is understandable why there is no linearity. At the frequency equivalent to the scan rate the phase angle is not zero and there is not a pure resistive response.

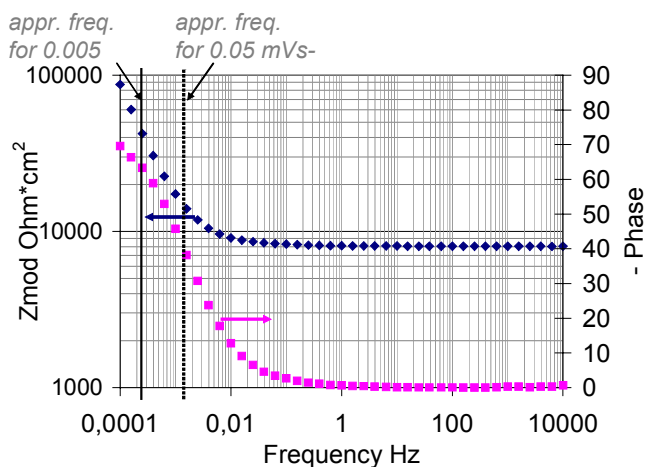


Fig. 4.3.24. EIS Bode plot on probe 6 o'clock, day 15, Viborg.

So even though it actually seems as if the corrosion rates from LPR and ER are in the same range there is a large uncertainty on the LPR. Furthermore, there is no hope to find a scan rate low enough, if the electrochemical response is e.g. dominated by diffusion. There will not be a purely resistive response at low frequencies. Therefore – and not due to IR drop – the LPR technique should not be used.

LPR data from the 7 plants seem to give “correct” corrosion rates in 2-3 plants especially in cases, where corrosion rate is increased for some reason. The risk of misinterpretation is, however, just too large. In conclusion the high scan rate does always give overestimated rates, while the slow scan rate in some of the plants give reliable results. The slow LPR data could be fitted to a realistic value, but if there is no indication of when not to trust them, the technique is not recommendable.

For the EIS technique in 4 out of 6 units the data gave corrosion rates in the correct range, but with a possible small overestimation equivalent to the results of the initial laboratory tests.

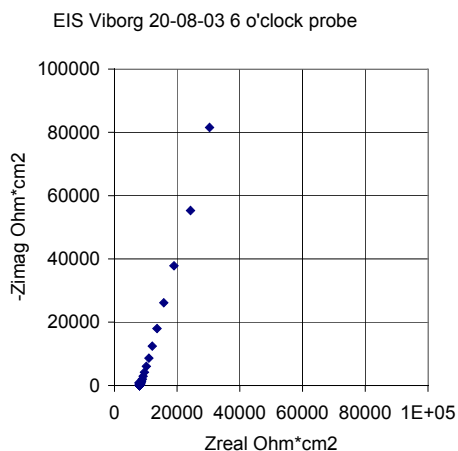


Fig. 4.3.25. EIS Nyquist plot on probe 6 o'clock, day 15, Viborg.

Fig. 4.3.25 shows the Nyquist plot corresponding to Fig 4.3.24 which is analysed as a very large semicircle giving a low corrosion rate $< 1 \mu\text{m/yr}$. The main problem with EIS is the long data acquisition time of several days, and that fitting is necessary to find a polarisation resistance from the obtained points. In the case of diffusion controlled corrosion a correct value might not be found.

Data from VEKS-Karlsunde in Fig. 4.3.26 illustrate a system where both LPR, slow LPR and EIS overestimated the corrosion rates (15-20 $\mu\text{m/yr}$) and where EIS data gave inductive semicircles. ER gave a corrosion rate of 1-2 $\mu\text{m/yr}$. From laboratory experiences it might be explained by crevice corrosion at the probe-teflon interface, but visual inspection of probes showed this idea to be wrong. At present there is no explanation for this behaviour, but it is probably related to the deposits formed on the probes.

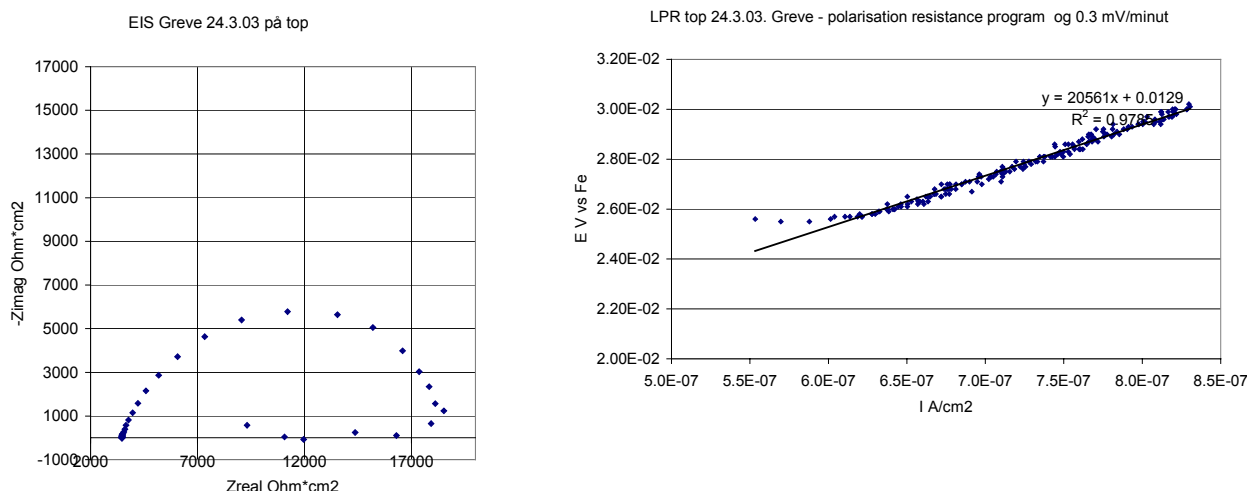


Fig. 4.3.26. EIS and LPR slow on 12 o'clock probe VEKS-Karlsunde.

Visual inspection of three-electrode probes after termination of the experiments showed a tendency to large differences in appearance of three identical steel rods in a probe. This might indicate that the techniques are destructive to the probes, and that corrosion or formation of deposits can be affected by the probe acting as reference electrode, counter electrode or working electrode. It might not be a problem if the same electrode configuration is kept, but this issue should then be emphasized.

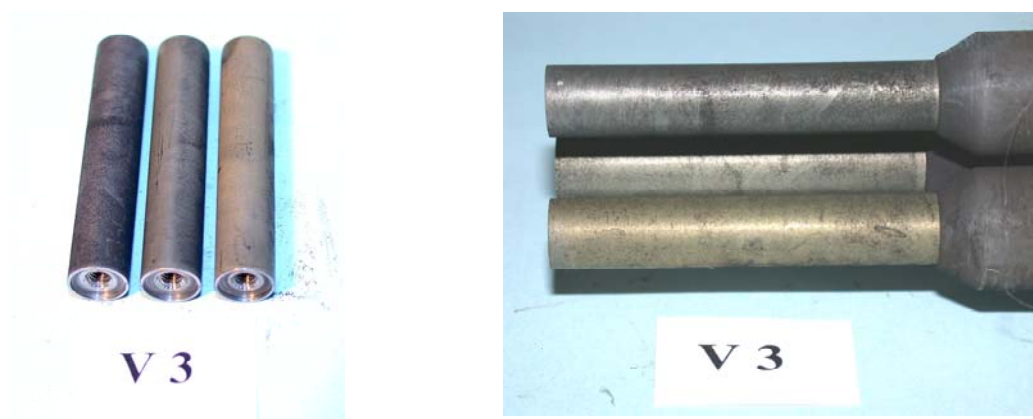


Fig. 4.3.27. Three electrode probes from VEKS-Karlsunde.

Based on comparison of high sensitive ER, chemical characterisation of the media, weight loss, and visual examination of probes from all 7 units it is found that the ER technique gives fairly correct corrosion rates. However, based on visual examination the rates may be slightly underestimated as compared to the district heating system materials since the iron foil in the ER probe is slightly more corrosion resistant than the carbon steel materials used for e.g. weight loss and electrochemical techniques. Based on field data the following evaluation of the techniques has been made.

Table 4.3.2. Comparative evaluation of performance of monitoring techniques in field units.

**The conductivity of 200-350 $\mu\text{S}/\text{cm}$ in Ballerup and the Lundbeck units differ from the other units (30-90 $\mu\text{S}/\text{cm}$).*

	ER	LOCOR	LPR	EIS	Weight loss	Media	Deposits
Odense	Good, low and high rates according to media	Good, low and high currents according to media	Overest., hysteresis, straight lines	To few data, Inductive	Good, high rates, severe localized and uniform corrosion	Non corrosive + very corrosive	Corr. products
VEKS	Good, low rates	Good, low currents	Overest., also with slow LPR, straight lines	Overest., Inductive	Good, higher than expected, uniform corrosion	Non corrosive	Yes
Viborg	Good, low rates, problem with data aquisition	Good, low currents, peaks during short term oxygen	Overest., but correct values with slow LPR, hysteresis	Good, large semi-circles	Good, low rates, small degree of pitting	Non corrosive, but with short term oxygen ingresses	No
Aalborg	Good, low rates	Good, low currents	Overest. with slow LPR, straight lines	No data	Good, low rates, uniform corrosion	Non corrosive	Yes
Ballerup	Strange, negative corrosion rates	Good, low currents	Overest., hysteresis	Good, large semi-circles	Good, low rates, uniform corrosion	*Non corrosive	Yes
Lundbeck cooling	Good, low rates	Good, low currents	Low rates with slow LPR, straight lines	Low rates, inductive	Good, low rates, uniform corrosion	*Non corrosive	No
Lundbeck heating	Good, high rates initially (80 $\mu\text{m}/\text{yr}$) going to lower rates	Good, high currents initially, low currents later	Slight overest. with slow LPR, high rates initially, lower later, straight lines	Slight overest., high rate equal to slow LPR, Depressed semi-circle	Good, fairly high rates from uniform corrosion.	*Corrosive initially due to large amounts of make-up water, later low corrosive	Black corrosion products

Discussion

It is evident that the risk of crevice corrosion do exist in the systems and that the LOCOR cell could be a way of detecting a given risk. From field data the general picture is a steady low current and high current peaks during e.g. oxygen concentration changes. The cell gives a characterisation of how localized corrosion reacts to changes in the media (oxygen, conductivity, pH), and data from ER measured in plant Odense and Viborg and pitting attacks on probes support the findings that these current peaks are in reality related to a localized corrosion attack. It has, however, been found that corrosion attacks on the crevice cell did not cover the entire anode surface, but only 1/5 or 1/10 of it, which means that the local corrosion rate cannot be found by dividing the current with the expected anode area. For future application smaller anode areas might be tested.

The probe techniques should have an acceptable life time and give a warning, if the probe is out of function. For the ER technique, the life time is defined by the corrosion rate, since for optimum sensitivity probes should be changed, when only half of the original thickness is left. This can easily be detected, but identifying whether the response is from severe localized attacks on the probe is presently not possible. In the actual units no serious localized attacks were found on the probes, indicating that general corrosion rates are measured on these. For the electrochemical techniques the 3-electrode probes have a risk of crevice corrosion in the probe itself at the connection between Teflon holder and probe. From laboratory data it had been seen that crevice corrosion would generate inductive semicircles in Nyquist plots. However in the case of e.g. VEKS-Karlsunde the probes do not seem attacked by crevice corrosion and this reason cannot be used to explain the inductive semicircles measured in this plant. Other reasons could be adsorption which would also generate inductive circles, but in any case the corrosion rate is overestimated also by EIS. For the crevice corrosion cell the lifetime is shortened, if it is exposed to strongly aggressive media for a longer period causing corrosion products to block up the glass membrane.

In case of the LPR technique it is actually feasible to measure in low conductivity water without problems with IR drop, but the problem becomes choosing a low enough scan rate and getting reliable data on a passive or film-covered metal. A system dominated by diffusion control reacts slowly and even at very low scan rates the corrosion rate is overestimated as compared to e.g. ER. It is doubtful if anything worthwhile can come out of LPR measurements in these systems. It might be that corrosion rates which seem to be correct can be determined, but when the basic criteria for the technique are not fulfilled, it should not be used. With the EIS technique corrosion rate can in most cases be determined with an acceptable accuracy, but the long duration of each measurement of almost 3 days makes it unfit for continuous monitoring.

High-sensitive ER technique gives fast and sensitive response also in the case of corrosion rates in the range of $0-1 \mu\text{myr}^{-1}$. The tests have shown that both high and low corrosion rates can be detected on the same probe by this technique and within a short measurement time of a few hours. The largest benefit is the continuous monitoring which is independent of temperature or media. Thereby many of the problems which e.g. electrochemical measurements suffer from and the long exposure time necessary for weight loss coupons are avoided.

Bacterial counts on coupons in field tests.

To achieve an indication of whether the monitored district heating systems were heavily affected by microbial growth and biofilm formation, two coupons from each plant were applied for biofilm analysis. The intention was to take the coupon placed in position 1 that is 12 o'clock position, and in position 12, which was the stagnation pipe mounted in 6 o'clock position. In Viborg this last coupon was not retrieved since the valve to fill the stagnation pipe had not been opened on mounting of the unit, and the probe had therefore not been exposed.

Transport containers made of polypropylene were autoclaved before use and filled with district heating water from the actual plant just before the coupons were removed from the unit and instantly transferred to the transport container. This procedure was chosen to ensure the less disturbed biofilm with the possible largest number of live bacteria on arrival to the microbiological laboratory. At arrival the deposits on the coupons were scraped off and the deposits conserved in formalin. Later the samples were homogenised, filtered, stained with DAPI and enumeration conducted by use of fluorescence microscopy. The results are given below as the average number of bacteria pr cm². Two independent counts have been made on each sample.

	Sample	cells/cm ²	Std. dev.
Ballerup	B3, position no. 3 – 12 o'clock	1,21E+05	2,5E+04
Ballerup	B8, position no 8 – 6 o'clock	5,14E+05	6,4E+04
Odense	OD1, position no. 1 – 12 o'clock	7,91E+05	2,16E+05
Odense	OD12, position no. 12 – 6 o'clock	2,08E+06	2,69E+05
VEKS	V1, position no. 1 – 12 o'clock	8,29E+05	2,43E+05
VEKS	V12, position no. 12 – 6 o'clock	2,47E+06	4,87E+05
Aalborg	AA1, position no. 1 – 12 o'clock	3,83E+05	1,17E+05
Aalborg	AA12, position no. 12 – 6 o'clock	7,88E+05	1,23E+05
Viborg	Vi- 1, position no. 1 – 12 o'clock	1,49E+05	6,06E+04
Viborg	Not retrieved		
Lundbeck heating	LV1, position no. 1 – 12 o'clock	5,58E+05	1,64E+05
Lundbeck heating	LV12, position no. 12 – 6 o'clock	3,64E+05	2,00E+05
Lundbeck cooling	LK1, position no. 1 – 12 o'clock	7,60E+05	2,87E+05
Lundbeck cooling	Lk12, position no. 12 – 6 o'clock	6,50E+05	1,56E+05

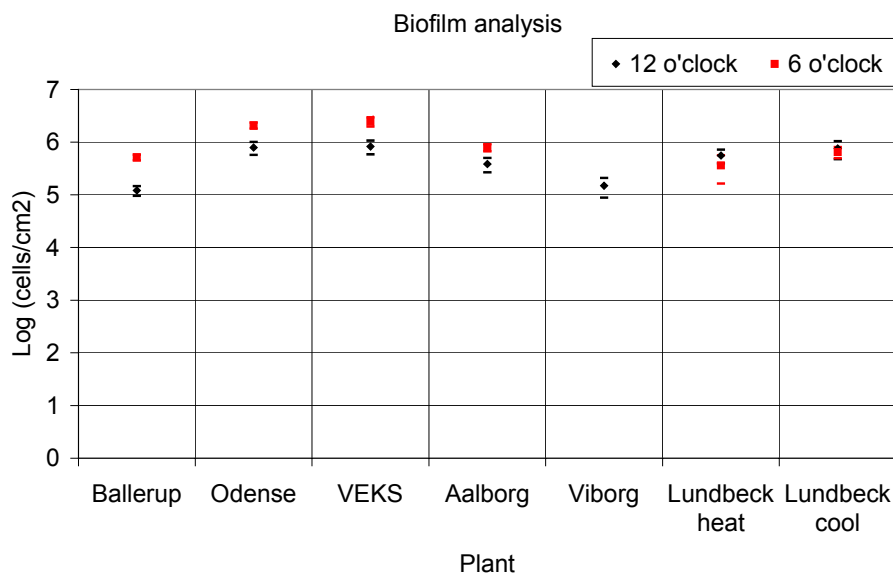


Fig. 4.3.28. Biofilm analysis in the Danish plants.

The results show that the number of bacteria on the different coupons is approximately the same 10^5 - 10^6 bacteria pr cm^2 , see Fig. 4.3.28. This is according to Professor Per Halkjær Nielsen (AAU) fairly low compared to counts in other Danish district heating systems, where 10^6 - 10^7 cells pr cm^2 is common. There are slightly more bacteria on the 6 o'clock probes in the stagnation pipe than in the top probes in the full flow, but the effect is not very strong. Odense and VEKS give the highest numbers, but still in the low range. The data support the overall findings from subproject 6A that the corrosion rates and specific attacks in this survey can be attributed to changes in chemical parameters due to e.g. make-up water addition, but also that there exists a risk of biofilm growth if organic matter is transferred to the systems.

Final laboratory test

A final test was made to examine whether the early choice of borax buffered simulated system water was unwise, and whether demineralised water pH adjusted with NaOH would give results that could help interpretation of field data. The unit was filled with approximately 30 L of N_2 -purged water of pH 9.82 and conductivity of $23.2 \mu\text{S}/\text{cm}$. The water was kept at 60°C and recirculated in the lab unit and after $1\frac{1}{2}$ months monitoring was initiated. At this point pH was almost unchanged (9.77) and the conductivity had increased to $87.9 \mu\text{S}/\text{cm}$. Monitoring by ER, crevice cell, EIS and LPR was carried out for one month on the unchanged system and afterwards followed one week of periodically forced oxygenation for one hour on day 27, 28, 31 (twice within 20 hours) and on day 34. In the end of the test pH had increased to 10.3. It seems strange that pH increased instead of decreased due to corrosion, and the value is not within the recommended 9.8 ± 0.2 , but actually in a range to even more facilitate passivation of steel. Conductivity had increased further to $155.9 \mu\text{S}/\text{cm}$. No monitoring of the media was applied, so at which time the change in pH appeared cannot be determined.

The crevice corrosion cell indicated no corrosion until oxygenation. For the first two oxygenation events crevice corrosion current increased, while for the following three it actually dropped during the one-hour oxygen ingress. In total the crevice corrosion current declined from day 28 to 35. This might either be due to a change of mechanism from local to uniform corrosion, or that the glass filter was filled with corrosion products hindering diffusion and slowing the reactions. Visual investigation of the probe showed a low degree of corrosion on the actual anode in the crevice cell, and deposition of corrosion products in the glass filter.

The ER technique responded with a very low corrosion rate (3-0.3 $\mu\text{m}/\text{yr}$) until the oxygenation started, and corrosion rate continued to increase up to 5 mm/yr until the probe responded with overload. Visual examination showed that the ER probe was penetrated by pitting.

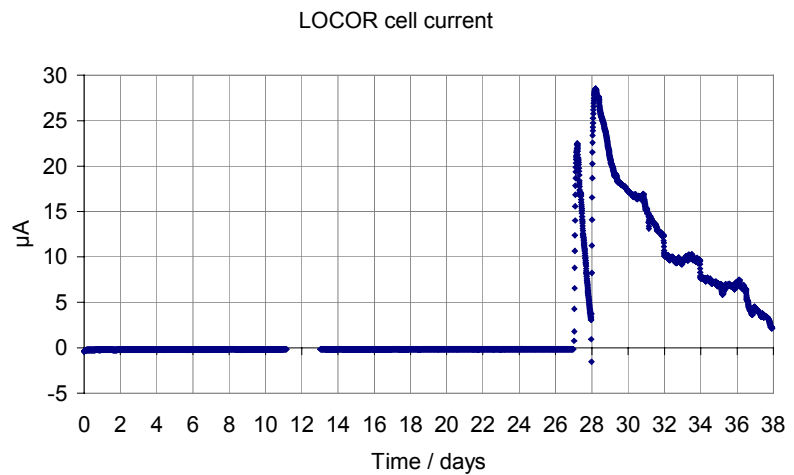


Fig. 4.3.29. LOCOR cell response.

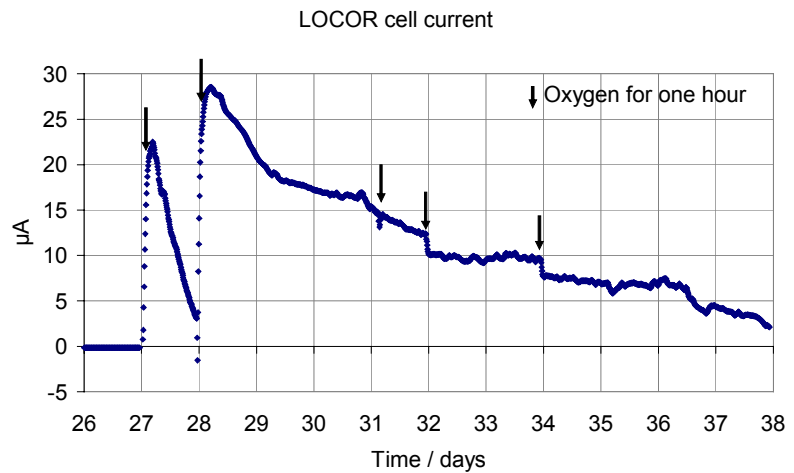


Fig. 4.3.30. LOCOR cell response for the final weeks.

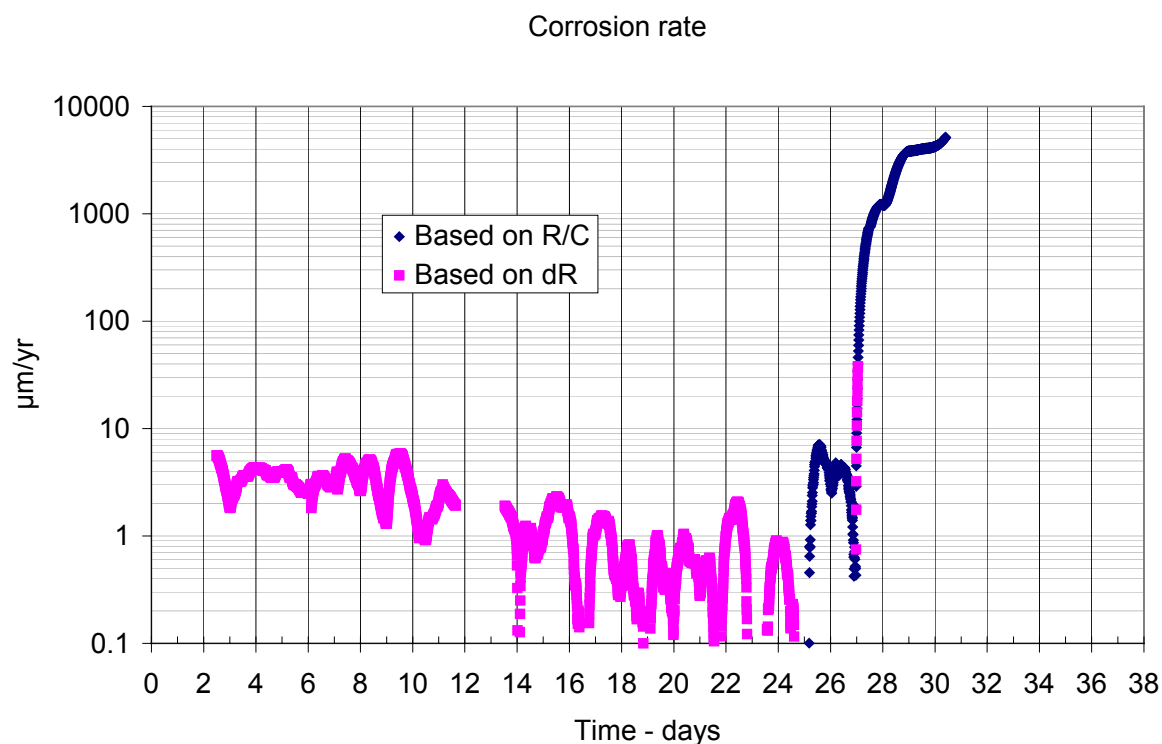


Fig. 4.3.31. ER corrosion rate.

The response from the electrochemical techniques indicated that the applied media and the prolonged exposure time indeed was more representative for the field data than the buffered media used in the initial lab tests. Visual examination of the corrosion attacks on the three electrode probes showed that these were severe with large amounts of voluminous corrosion products appearing similar to those found at Odense.

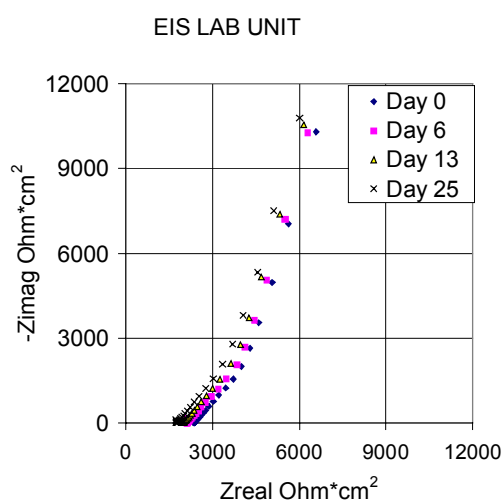


Fig. 4.3.32. EIS Nyquist plot from first month.

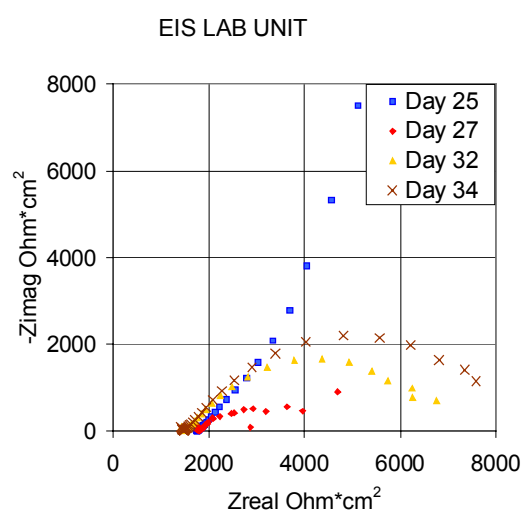


Fig. 4.3.33. EIS Nyquist plot from the final weeks.

EIS data was dominated by effects from the low conductivity water as documented in the early lab tests, and finite diffusion effects indicating deposits on the metal.

For the first month of monitoring the response was unchanged, except for a small decrease in solution resistance as a consequence of the small increase in conductivity. Corrosion rates could, however, not be determined from these curves by fitting, as the number of points at low frequencies was too low. The phase angle moving above 45° at low frequencies (Bode plot) indicates that very large semicircle ($>400 \text{ kOhm}\cdot\text{cm}^2$) would appear in Nyquist plot, if low frequencies had been reached. After oxygenation the response changed to small depressed semicircles in Nyquist plot. In Bode plots it is clear to see that the phase angle response is very different than before oxygenation and that solution resistance again decreases, thus conductivity increases. Estimation of polarisation resistances in these curves give 5500, and 7000 $\text{Ohm}\cdot\text{cm}^2$ at days 32 and 34 calculated to corrosion rates of 55 and 43 $\mu\text{m}/\text{yr}$.

The LPR data are during day 0 to 26 stable, but with the same type of nonlinearity as found in the district heating plants. The current crosses 0 and estimated R_p is around 18.000 $\text{Ohm}\cdot\text{cm}^2$. The measurements at day 27 and 34 give more linear curves giving R_p values of 1500 to 6000 $\text{Ohm}\cdot\text{cm}^2$ (200 to 49 $\mu\text{m}/\text{yr}$), which is in the same range as the EIS curves. Comparison of these data with ER data again shows that the corrosion rate in deaerated system cannot be determined by LPR nor EIS (to few low frequency points), but in the corroding system these techniques do react to the changes and generate a very different response, not so different from the corrosion rate found by ER.

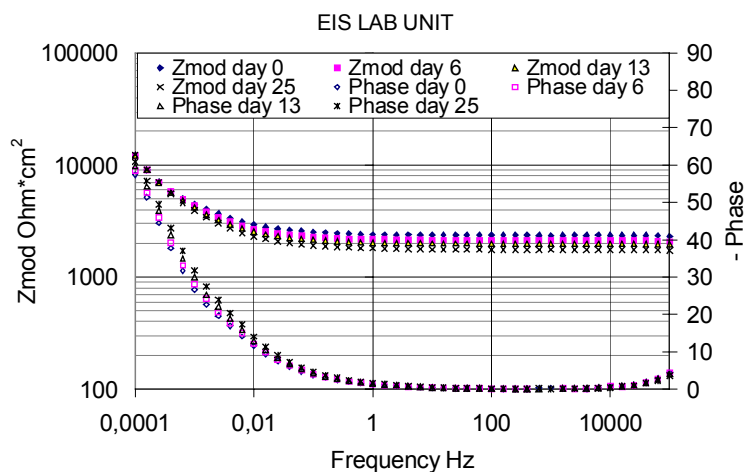


Fig. 4.3.34. EIS Bode plot from first month.

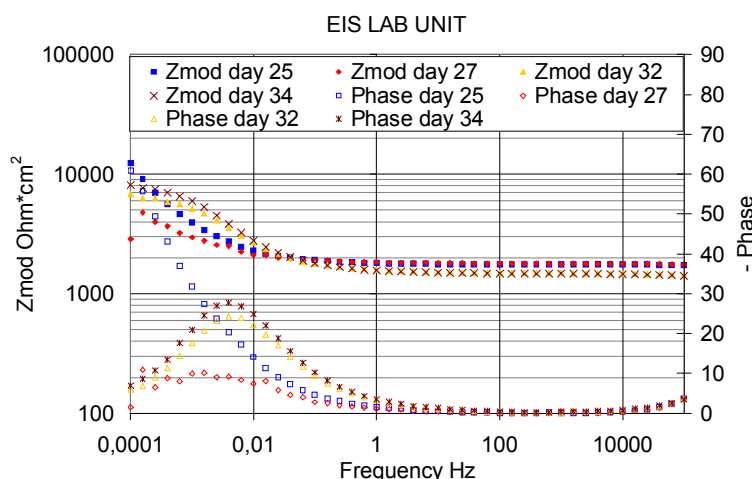


Fig. 4.3.35. EIS Bode plot from the final weeks.

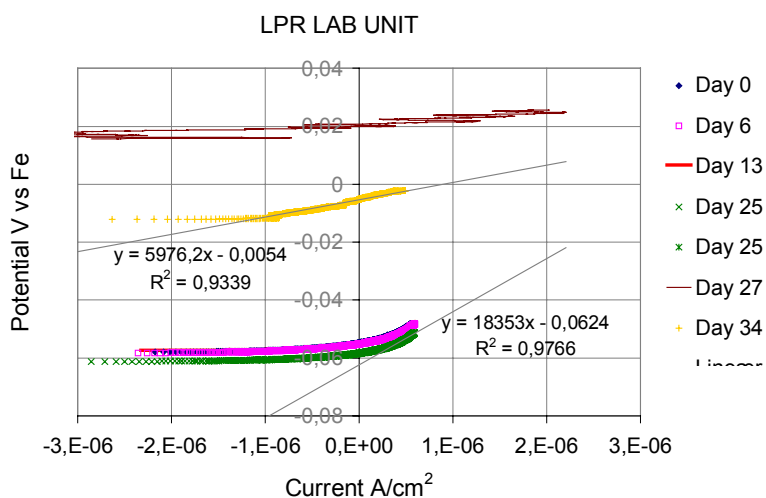


Fig. 4.3.36. LPR curves.

To conclude the use of NaOH adjusted water was actually stable enough for simulating system water, and the experiments illustrated the same type of measurement problems as seen in the field units. The test included an unrealistically strong oxygenation, which however did give responses not so very different from Odense.

The overall goals of the final laboratory test combined with the field tests were

- *to characterise the performance of the various techniques in different media supplementary to field data – performance of EIS and LPR.* The response does change as corrosion rate changes, but the reliability is not good enough and LPR is not applicable. EIS does give sensible results, but with a too long measurement time. The reliability is better in more corrosive media.
- *to correlate corrosion rates measured with ER with EIS in district heating water.* A fairly good correlation was found by adjusting the B value to approximately 15 mV, but overestimation still occurred or no corrosion rate could be found from EIS.
- *to possibly improve LPR by e.g. slower scan rates.* Better results can be obtained, but since the linearity is still not fulfilled and there is not a simple activation controlled mechanism, the direct correlation between R_p and corrosion rate becomes doubtful. Passive materials are just difficult to monitor with LPR.
- *to investigate the effect of low oxygen ingress, aggressive ions, and conductivity on the crevice corrosion cell current.* The LOCORR cell reacts quite fast, but if the conductivity is low the range will be very small and minor oxygen ingresses will only generate a small current. Extended time with high oxygen levels can destroy the sensitivity of the probe. The effect of aggressive ions has not been investigated.
- *to investigate whether design and placement of probes can improve the sensitivity of ER to localized corrosion.* The partially covered ER probes were not significantly attacked by crevice corrosion. However, some localized corrosion was found just at the borderline between bare and covered surface - again supporting the importance of a low conductivity making the range of localized elements very small.
- *to characterise the practical stability of the various techniques.* The ER prototype probe performed well and the extreme localized attack in the lab test gave a warning by turning into an overload signal. The polymer materials performed fine in the systems. The LOCORR functioned well but can be affected by corrosion products, which cover the frit and hinder diffusion. Corrosion did not take place on the entire anode surface, but only on the edges of the surface. A few of the three-electrode probes seemed attacked by crevice corrosion after 1 year exposure, probably due to the fact that it was difficult to tighten them without overdoing it. Otherwise the design was o.k. The weight loss probes were slightly more attacked at the mounting screws, but performed o.k.

Results from geothermal district heating systems in Iceland

Characteristics of geothermal systems

Most district heating systems in Iceland make use of low temperature geothermal fields. The geothermal water is used directly both as hot tap water and for heating. The usual temperature for distribution is 70-80°C. In high temperature geothermal fields the temperature is 150-200°C and the heat is then transferred to fresh water, which is deaerated by boiling and pumped to consumers. In some cases a small dose of geothermal steam containing H₂S is mixed with the water for reacting with the oxygen that may be absorbed in water tanks on the way to the consumers. The major part of the distribution system is a single pipe system.

Chemical composition of geothermal water

The geothermal water is in origin rainwater, which seeps down into the bedrock and is heated by the hot rocks. Minerals dissolve from the rocks and most often, the solubility increases with increased temperature. Thus, the low temperature water normally has a content of dissolved solids of 200-400 mg/l, whereas the total dissolved solids in high temperature fluids typically exceeds 1.000 mg/l. Geothermal water is normally free of dissolved oxygen, but water from a few boreholes may contain a limited amount of oxygen if the sulphide content and the temperature of the water is low. Furthermore, oxygen may enter the system e.g. in storage tanks.

Table 4.3.3 shows the chemical composition of the fluids used in this research. At three places the water is geothermal with origin in different wells and the fourth water type is heated fresh water.

First there is geothermal water from Reykir, a low temperature area right outside Reykjavik. The measurements took place in the distribution network at the Icelandic Centre for Building Installations. Secondly, there is geothermal water at Bolholt pumping station in Reykjavik. The water chemistry is stable and the water is distributed directly to the consumers without entering a storage tank. No oxygen is detected in the system. The third water type is geothermal water at Oskjuhlid pumping station in Reykjavik. The water contains limited amount of dissolved oxygen entering the water in the storage tank right beside the pumping station. The ingress of oxygen causes fluctuations in the sulphide concentration as the sulphide and oxygen react forming sulphate through intermediate sulphur compounds, such as sulphite and thiosulphate. The fourth water type is heated fresh water in Keflavik from Hitaveita Sudurnesja. The water is oxygen free, but may contain a detectable amount of sulphide from geothermal steam.

The main differences in the water chemistry between test locations is in pH, conductivity and the concentration of dissolved oxygen, sulphide, silica, magnesium, calcium and chloride. The pH of the heated fresh water in Keflavik is lower than of the geothermal water, the content of magnesium, calcium and chloride is higher and the silica and sulphide concentration is lower. Less differences are found between the geothermal water types, but dissolved oxygen is only detectable in Oskjuhlid and the conductivity is higher in Bolholt.

Table 4.3.3. The chemical composition of the water.

	Reykir	Bolholt	Oskjuhlid	Keflavik
Temperature, °C	80	80	80	105.4
pH at 25°C	9.6	9.5	9.5	8.9
Conductivity, µS/cm	206	345	200	153
Dissolved oxygen, mg/l	<0.003	<0.003	0.05-0.08	<0.003
Sulphide, total, mg/l	1.0	0.5-0.9	0.5-0.9	0.08
Sodium, mg/l	44.6	59	43	34.3
Potassium, mg/l	0.9	2.0	0.9	1.5
Calcium, mg/l	2.1	3.4	2.5	8.1
Magnesium, mg/l	0.003	0.01	0.01	6.9
Chloride, mg/l	14.4	56	20	74.7
Sulphate, mg/l	16.2	21	18	11.2
Total carbonate, mg/l	16	12	15	6.0
Silica, mg/l	94.3	150	88	13.0

Online oxygen measurements

Online oxygen measurements have not been practical due to the presence of sulphide in the systems. Thus, the concentration of dissolved oxygen has been measured by CHEMets self-filling ampoules for colorimetric analysis (0-20 ppb, 0-100 ppb and 0-1.000 ppb) during the research period. In late January 2004 Oxyguard® in Denmark managed to present a possible solution to the measuring problem, Oxyguard® PPB 6150 with a special DO probe type CD01. A test with this equipment has been running for two months and comparison made to measurements by CHEMets ampoules. The results are shown on Fig. 4.3.37. The results seems reliable for the first 7-10 days but after that the Oxyguard® equipment shows much lower values than the ampoules. After recalibration of the instrument the values are higher again. According to Oxyguard the calibration must be carried out more often in the beginning of the measuring period, but within longer time intervals later on. This is presently being tested and will be reported in the Ph.D. report by Sonja Richter in the end of 2004.

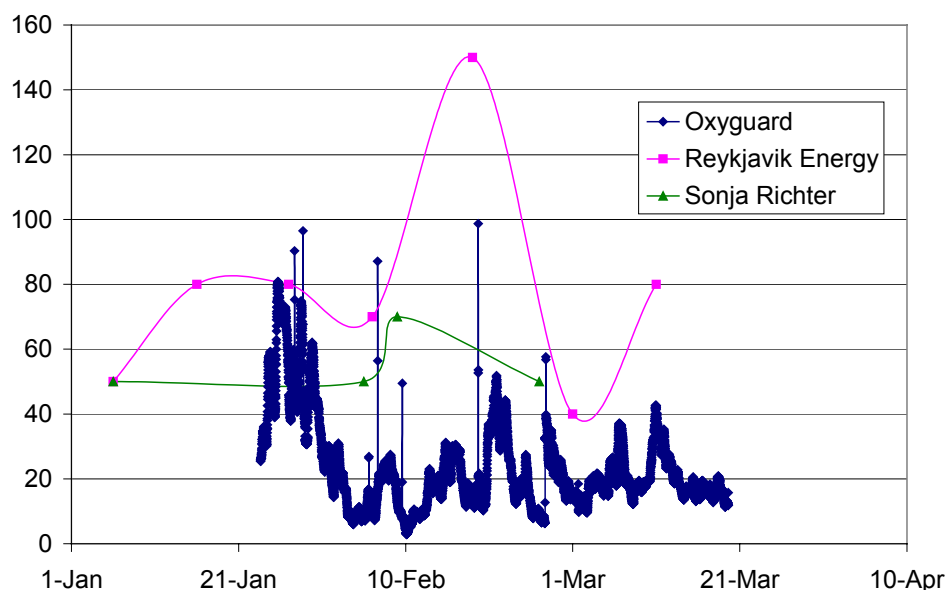


Fig. 4.3.37. Oxygen measurements in Oskjahlid. Online measurements with Oxyguard® PPB 6150 with special DO probe type CD01, and other measurements with CHEMets self-filling ampoules for colorimetric analysis (0-20 ppb, 0-100 ppb and 0-1000 ppb).

Comparative studies on reliability of the electrochemical techniques in geothermal water

After some pre experiments in Icelandic geothermal water, comparative studies on the reliability of the electrochemical techniques in geothermal water were carried out³². Former studies in 1999³³ had shown that conventional LPR and EIS methods did not provide reliable estimates on the corrosion resistance, but more information was gained from Tafel polarization curves. In the present experiment the techniques were tested in more details with a wide range of scan rates. The metal coupons were steel 37.

The applied techniques were linear polarisation resistance (LPR), electrochemical impedance spectroscopy (EIS) and Tafel polarisation.

The first experiments were performed in a corrosion cell in the laboratory. see Fig. 4.3.38 and later in a simple test rig simulating in-situ measurements, see figs. 4.3.39-40. The water was from Reykir, see table 4.3.3.

Laboratory

The laboratory tests were conducted in a 1000 ml cell, with a three-electrode setup. The working sample was a cylindrical carbon steel rod, with diameter 9 mm and height 12 mm and a total area of

³² Norskov, L., Comparative studies of the reliability of electrochemical techniques in geothermal water, IBRI, Keldnaholt, IS-112 Reykjavik, ICELAND, 2003.

³³ Thorarinsdottir, R.I. Corrosion of copper and copper alloys in geothermal district heating water containing sulphide, No. 85, IBRI, Keldnaholt, IS-112 Reykjavik, ICELAND, 2000.

4 cm². The reference electrode was a saturated calomel electrode and the counter electrode a carbon rod. Hot tap water ran continuously through the cell with a constant flow of 5 ml/s.

Tafel polarisation scans were run with scan rates in the range of 4-0.05 mV/sec. The samples were polished (320, 500 and 1000 grit) immediately before exposure and exposed to the solution for 30 minutes before the Tafel polarisation. The test was run with a polarization of ± 500 mV vs. SCE starting at the OCP.

For the LPR measurements the reference electrode was changed to be a steel rod same as the working sample as the calomel electrode did not seem stable in the environment. Cyclic polarisation scans were conducted at scan rates ranging from 0.01-0.0005 mV/sec. The polarisation was ± 15 mV vs. OCP.

The EIS measurements were set with frequencies ranging from 100.000 Hz to 0.01 mHz, 5 points per decade. The amplitude of the measurement was 10 mV. The EIS measurements were stopped after two days having reached the frequency of 0.04 mHz.

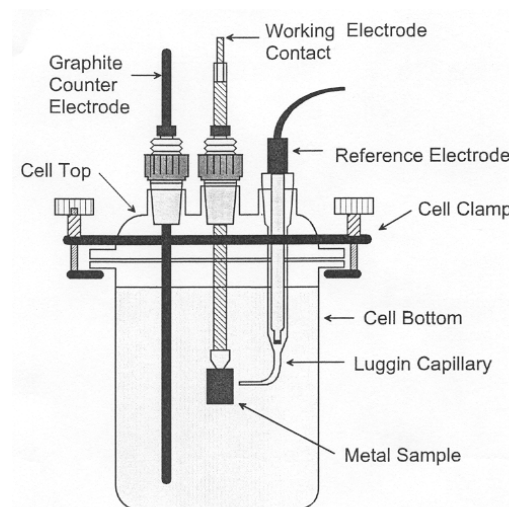


Fig. 4.3.38. Test setup.

Test rig

The test rig consisted of 8 rows of 1 1/4" iron pipes (length 1 m) where a plug can be inserted either in the middle or at the end of the pipes, see figs. 4.3.38-39. Weight loss coupons and three electrode probes for electrochemical measurements were inserted in the rig. The probes used were made of nylon with 3 carbon steel rods screwed in, with diameter 5 mm and length 6 mm and a total area of 1.14 mm². The water velocity was approximately 0.5 l/min.

The weight loss coupons were of steel 37, 50 mm by 25 mm by 1 mm. They were degreased with acetone and weighed to the nearest 0.1 mg before exposure. The test periods were 4, 8 and 12 weeks, respectively. After exposure the coupons were cleaned and weighed according to ISO 8407. The electrodes were polished with sandpaper grit 320, 500 and 1000 and degreased with acetone before exposure.

OCP measurements started immediately after the installation of probes and after five days of exposure LPR and EIS measurements were carried out.

LPR was carried out with scan rates ranging from 0.5 mV/sec – 0.0001 mV/sec, ± 10 mV and ± 20 mV from OCP. EIS was performed with the same settings as in the laboratory.

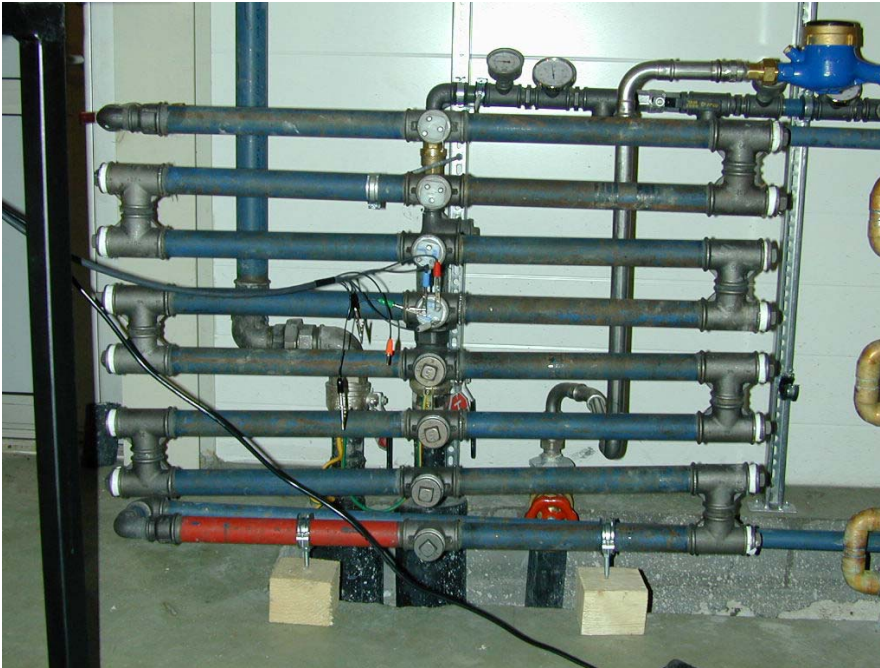


Fig. 4.3.39. The test rig.

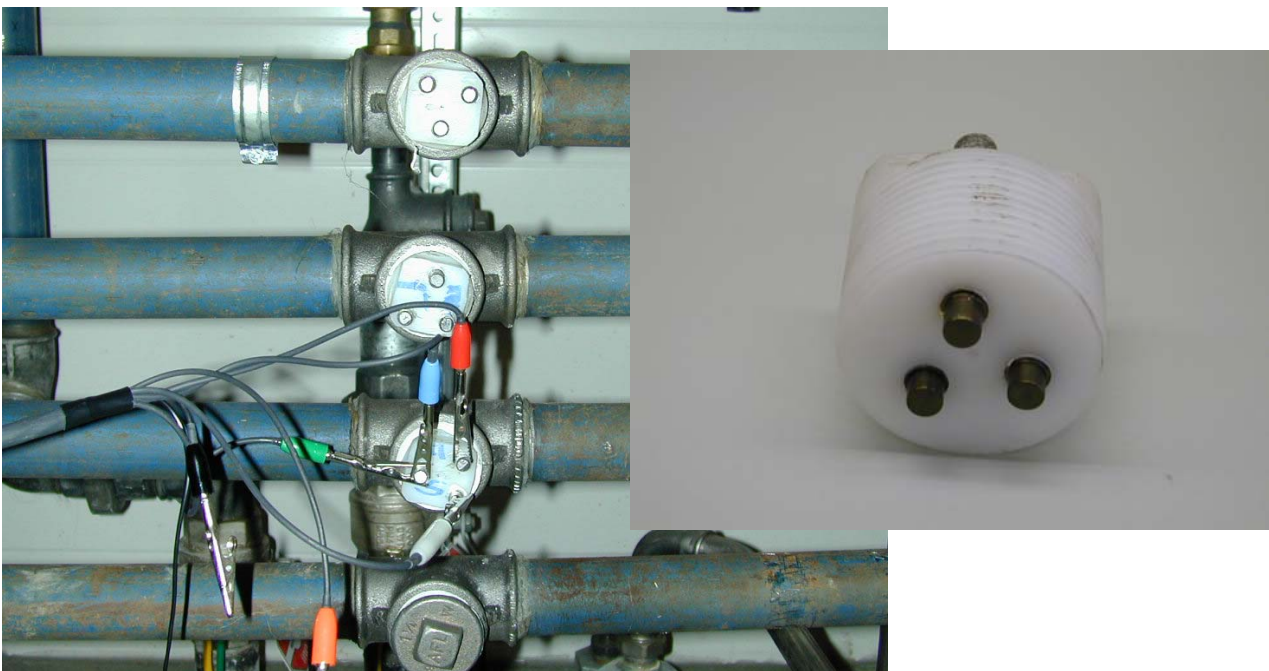


Fig. 4.3.40. Three electrode test probes.

Results

The results from the LPR measurements in the laboratory showed corrosion rates in the interval 10-14 $\mu\text{m}/\text{year}$, which is approximately ten times higher than expected in oxygen free systems. Moreover, it did not decrease with decreased scan rates as expected. Thus, these results were not reliable. This could be either due to an unstable reference electrode or that the corrosion cell has

not been completely tight. Oxygen entering the system will react with sulphide, but will also react with iron increasing the corrosion rate.

The LPR from the test rig was much more convincing in spite of non-linear polarisation curves with hysteresis. The corrosion rates decreased with decreased scan rates from 70-90 $\mu\text{m}/\text{year}$ at 0.5 mV/sec to 1-2 $\mu\text{m}/\text{year}$ at 0.0005 mV/year which was close to the results from weight loss coupons. Fig. 4.3.41 shows a typical LPR plot, which is similar to those observed in the Danish district heating systems.

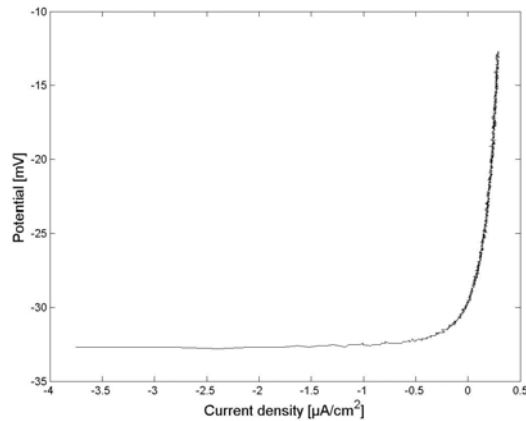


Fig. 4.3.41. A typical LPR plot from the geothermal systems.

The results from EIS measurements were not consistent. In some tests convincing corrosion rates were obtained but not in others. The measured corrosion rates were in the range 1-8 $\mu\text{m}/\text{year}$. The Nyquist plots showed diffusion control and were often distorted and difficult to interpret, see Fig. 4.3.42. Moreover, one test could take a couple of days.

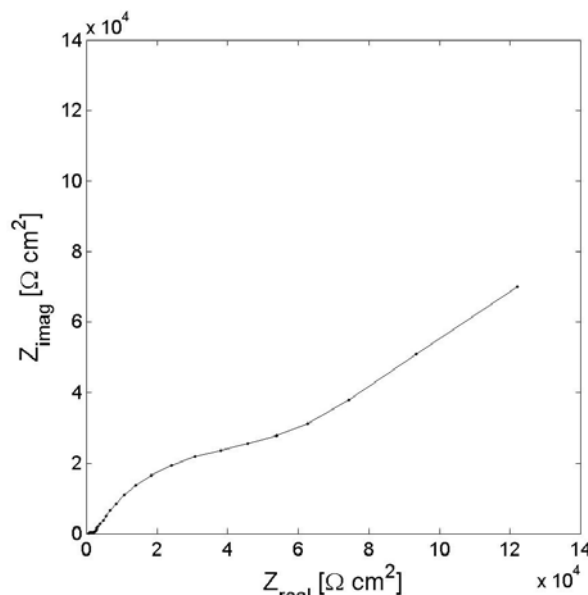


Fig. 4.3.42. A typical Nyquist diagram for carbon steel in the district heating systems. The diagram shows diffusion effects.

The Tafel curves did not provide reliable estimates of the corrosion rate due to non-linear Tafel slopes related to potential hysteresis and diffusion control of the anodic reaction.

Field tests

Field experiments were carried out in two stations in Reykjavik, *Bolholt* and *Oskjuhlid* and in one station on Reykjanes peninsula, *Keflavik*. A typical test setup is shown on Fig. 4.3.43. The first measurements were done on identical probes as shown in Fig. 4.3.39, but larger probes constructed at DTU with 9.2 cm² area were used in later experiments, see Fig. 4.3.44.



Fig.. 4.3.43. Corrosion test unit set-up at Oskjuhlid.



Fig. 4.3.44. Three electrode probe constructed at DTU.

LPR was mainly performed with equipment from Gamry, but in Oskjuhlid also with SmartCET instrument from Intecorr.

Gamry was set to a scan rate of 0.001 and 0.0005 mV/sec, respectively and the polarisation was ± 10 mV versus OCP. The SmartCET instrument is not adjustable and the LPR are preset to ± 25 mV and 0.5 mV/sec. According to prior results from the district heating systems this is too high a scan rate for reliable results. EIS was run on frequencies from 100.000 to 0.0001 Hz, ± 10 mV versus OCP.

Weight loss coupons of carbon steel, 25 mm by 50 mm by 1 mm, were used for comparison of the corrosion rate. They were cleaned with acetone and weighed accurately before exposure. The exposure period was 3 and 6 months, respectively. They were then dried, cleaned and weighed according to ISO 8407 in hydrochloric acid with hexamethylenetetramine.

Bolholt station

The results from Bolholt station is shown on Fig. 4.3.45. The weight loss measurements showed only 1 $\mu\text{m}/\text{year}$ and the LPR and EIS measurements showed even lower corrosion rates (0.2-0.7 $\mu\text{m}/\text{year}$). The measurements were stable as expected as the water chemistry is known to be stable in the station. Good correlation was observed between both the LPR measurements and the EIS results.

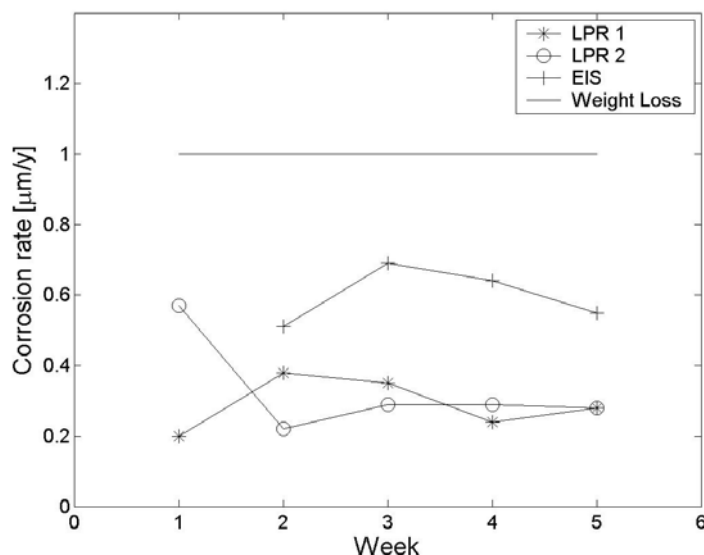


Fig. 4.3.45. The results from Bolholt station. LPR denotes the scan rate 0.001 mV/sec and LPR2 0.0005 mV/sec.

Oskjuhlid station

The corrosion rate is higher in Oskjuhlid due to the presence of dissolved oxygen and it varies much more because of fluctuations in the oxygen and sulphide content of the water. Though, there is a good consistency between all monitoring methods in Oskjuhlid as shown in Fig. 4.3.46. The higher values in the start of the period can be explained by higher oxygen concentrations in the beginning of the period (appr. 150 ppb), which was much lower (10 ppb) in the rest of the period. The weight loss measurements showed 5-17 $\mu\text{m}/\text{year}$. Earlier tests have shown 25-40 $\mu\text{m}/\text{year}$ which can be related to higher oxygen concentrations of the water up to 300 ppb.

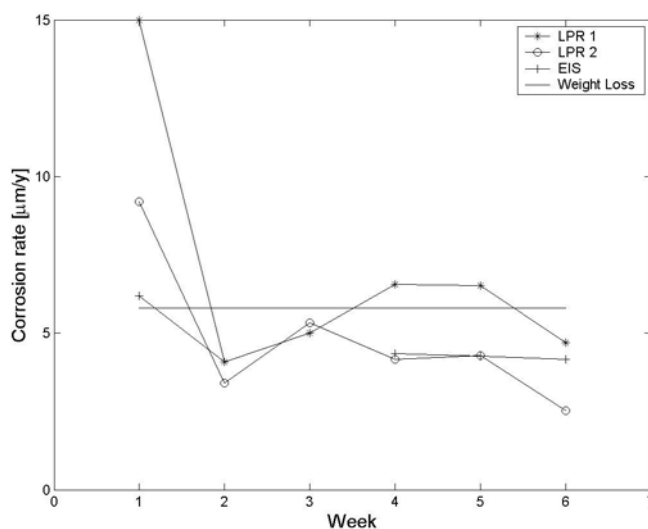


Fig. 4.3.46. The results from Oskjuhlid station. LPR denotes the scan rate 0.001 mV/sec and LPR2 0.0005 mV/sec.

Keflavik station

The results from the heated water at Keflavik are shown in Fig. 4.3.47. The weight loss measurements showed 1.1 $\mu\text{m}/\text{year}$ and the LPR measurements resulted in lower values, approximately 0.3-0.7 $\mu\text{m}/\text{year}$, while the EIS was 2.2 $\mu\text{m}/\text{year}$.

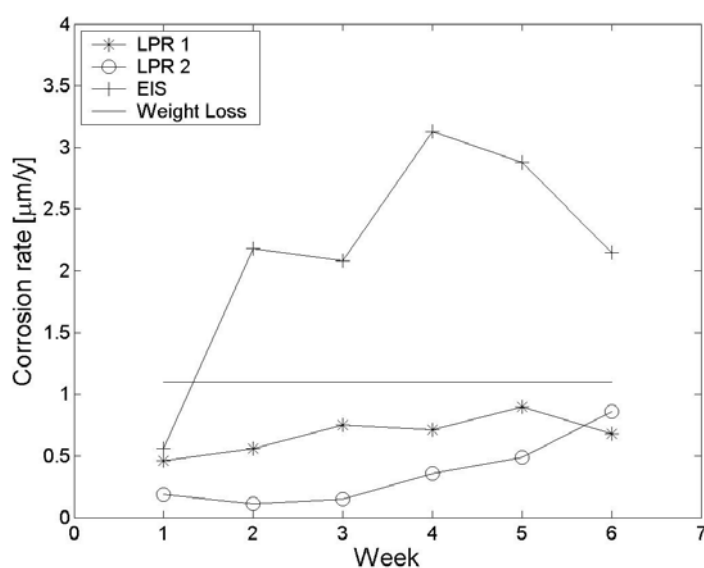


Fig. 4.3.47. The results from Keflavik station. LPR denotes the scan rate 0.001 mV/sec and LPR2 0.0005 mV/sec.

ZRA-measurements

ZRA measurements were done with the LOCOR cell developed by FORCE technology and also with a two electrode probe, where one electrode was copper and the other steel 37. The current was measured using a Wenking Laboratory Potentiostat Model LB 81 M. Measurements were logged every second by Campbell Scientific datalogger CR510.

Both cells reacted to changes in the oxygen level, see figs. 4.3.48-49. After six months of service the LOCOR cell got cloaked up with corrosion products and the measurements were not longer reliable.

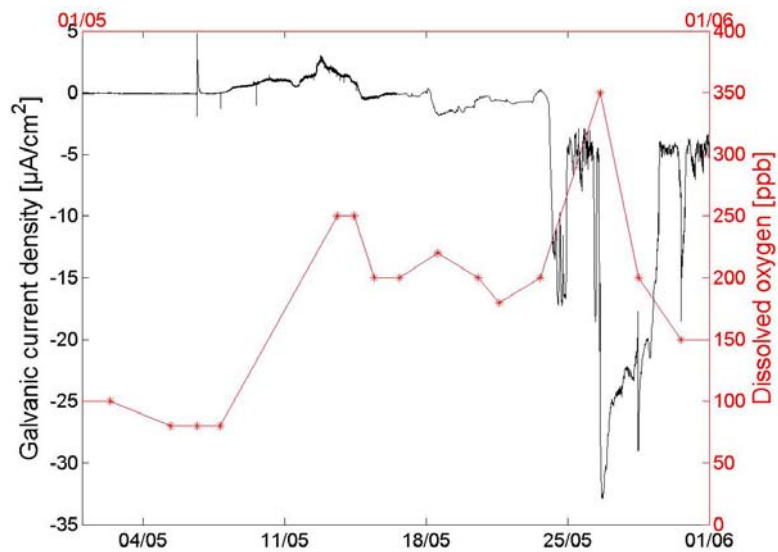


Fig. 4.3.48. Results from the LOCOR cell together with oxygen measurements.

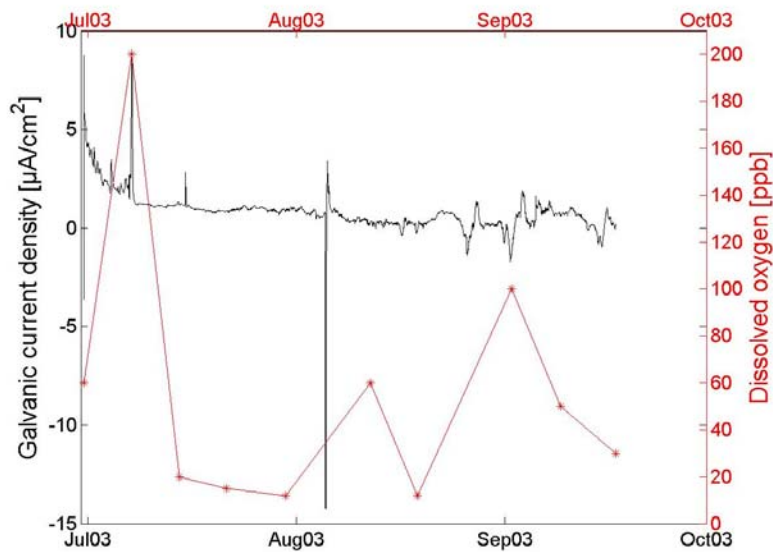


Fig. 4.3.49. Results from the copper/iron cell together with oxygen measurements (ampoules).

Electrical resistance

The ER measurements in Oskjuhlid station resulted in convincing results, the corrosion rate ranging from 10-20 $\mu\text{m}/\text{year}$ and closely following the oxygen content measured in the water, see Fig. 4.3.50.

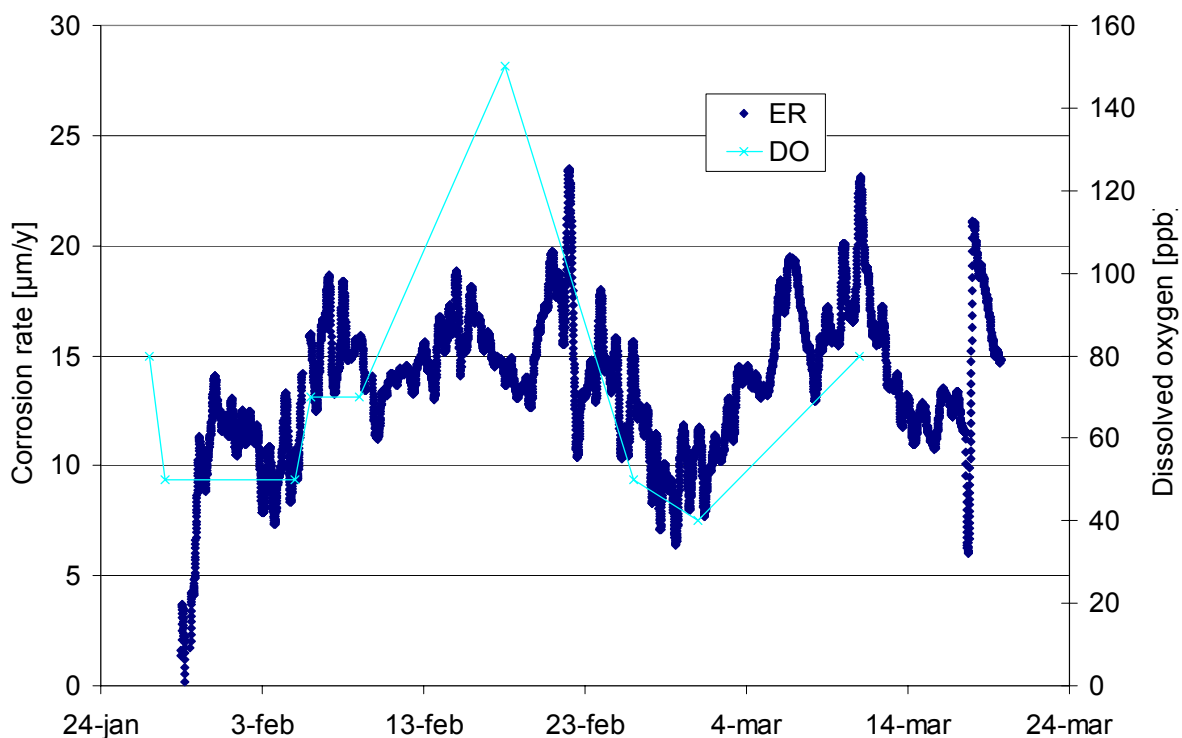


Fig. 4.3.50. Results from the ER measurements.

Electrochemical noise

The electrochemical noise measurements by SmartCET[®] also reacted promptly to oxygen fluctuations, see Fig. 4.3.52 and the pitting index is normally in the transition zone, indicating that the iron probes are prone to pitting. Examination of the electrodes confirmed this, see Fig. 4.3.51.

The LPR measurements by the SmartCET[®] instrument resulted in too high values, see Fig. 4.3.53 and table 4.3.4, which is related to the preset high scan rate. The scan rate can not be altered in the present model.



Fig. 4.3.51. Probes after a period of increased oxygen in Oskjuhlid station.

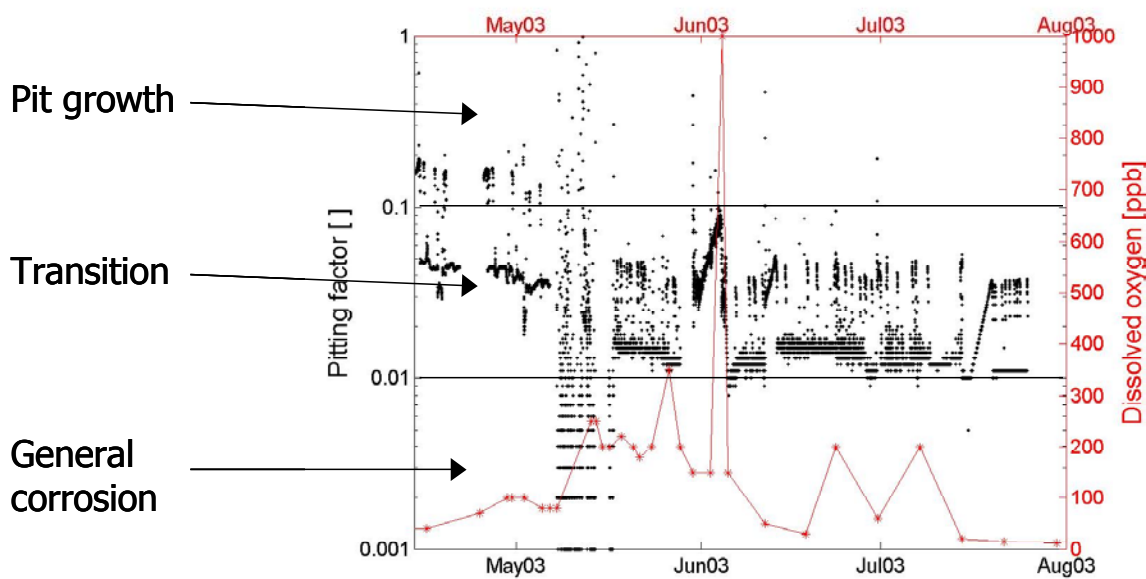


Fig. 4.3.52. Pitting factor by SmartCET[®] from Intercorr and oxygen measurements in Oskjuhlid station.

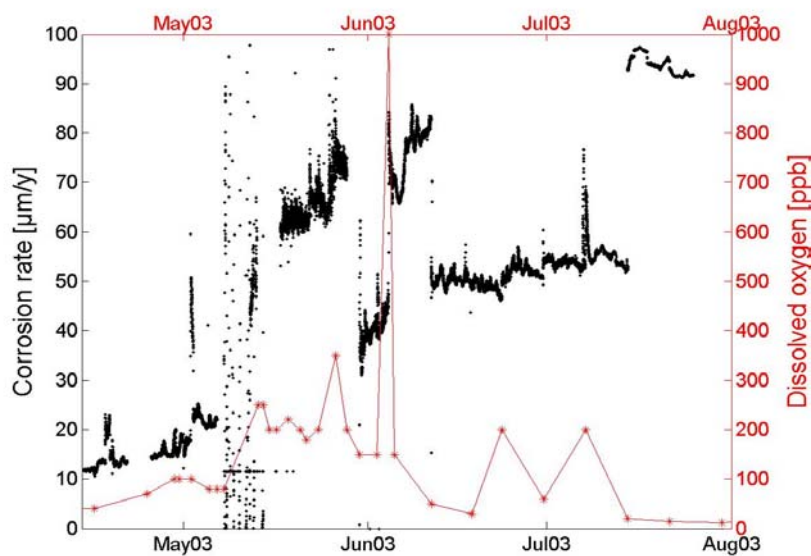


Fig. 4.3.53. Corrosion rate monitored by SmartCET[®] from Intercorr and oxygen measurements in Oskjuhlid station.

Table 4.3.4. Comparison of corrosion rate in Oskjuhlid station obtained with different monitoring method.

Method	Period	Corrosion rate (µm/year)
LPR – Gamry	June – July 2003	4-5
LPR - SmartCET [®]	June – July 2003	63
ZRA- LOCOR cell	May 2003	12
ZRA – Fe/Cu	July-Sept. 2003	11
Weight loss	2003	5-17

Conclusions from the Icelandic part

The results from the Icelandic geothermal systems imply applicability of the LPR technique as a quality control measure in a sulphide containing water distribution system in spite of non-linear polarisation curves with hysteresis. The scan rate has to be kept low 0.005 mV/sec, which means that each measurement takes several hours. Hence, the method is not optimal for online monitoring, but together with ZRA or EN it can be recommended for corrosion control.

ZRA measurements readily responds to changes in the environment, e.g. the main corrosion factor, oxygen ingress. Both the LOCOR-cell from FORCE Technology and a simple copper/iron probe can be used. EN measurements also responds to changes in the environment and could assess localized corrosion.

ER measurements are also a possibility for online monitoring of corrosion rate, the results were convincing and the corrosion rate measured followed closely the oxygen concentration.

The application of the EIS technique is considered questionable since consistent results were not obtained. In some EIS tests accurate corrosion rates were obtained, but not in others. The Nyquist plots showed diffusion control at low frequencies and were often distorted and difficult to interpret. One measurements can take several days and the system cannot be considered stable during so long time, hence the method is not recommendable for online monitoring.

Weight loss measurements can always be used as a quality measure and/or once in a while for checking the online methods.

Conclusion

In summary the Danish and Icelandic results points to the importance of testing corrosion monitoring techniques in the actual media.

The water in the systems is of high quality resulting in low corrosion rate for both uniform and localized corrosion of carbon steel. The corrosion rate is highly affected by environmental changes such as pH decrease, increasing conductivity and increasing oxygen content. Deaeration of make-up water must in general be recommended. However, increased oxygen content in a short time range is not very critical, if the other environmental parameters like conductivity and pH do not change, but can induce pitting. It can furthermore be concluded that continuous monitoring is necessary to detect these variations in corrosion rate and make-up water quality.

The electrochemical technique LPR generally overestimate corrosion rates in the Danish systems, and it cannot generally be recommended for district heating systems. However, the Icelandic measurements at very low scan rates resulted in reliable data. EIS gave more reliable data in the Danish systems, but not always in the Icelandic geothermal systems. Though, the measuring time is several days and the analysis is complicated. Fine results have been achieved with high-sensitive ER technique from MetriCorr independent of media type and sensitive to low rates. However, with this technique there is no quantification of degree of localized corrosion. This is possible with the crevice corrosion current measurement with the LOCOR cell from FORCE TECHNOLOGY, which has performed well and reacted within minutes to the environmental changes. Also ZRA

measurements with a copper/iron probe gave reliable results in the Icelandic systems. Off-line monitoring with weight loss probes have supported the findings, but requires minimum 3-6 months of exposure time to give reliable results.

Future plans

The final results has been presented to the Danish District Heating Association and participating Danish district heating industry at a meeting on March 23rd 2004 as well as at the 13th Nordic Corrosion Conference in Iceland April 2004. Furthermore, the obtained knowledge on corrosion monitoring techniques was communicated to young Nordic researchers at a Ph.D. course financed by NORFA in Iceland, April 2004.

For the benefit of the Danish district heating industry the obvious future project would be a cooperation between Danish Technological Institute, MetriCorr, DTU and FORCE Technology combining monitoring of microbially induced corrosion with continuous corrosion monitoring in the form of high sensitive ER and the LOCOR cell. The Nordic network has been beneficial for the participants and cooperation is expected to continue in future projects within this or other fields.

Sonja Richter, a Ph.D.-student at the University of Iceland will finish her Ph.D.-project in late 2004. She is performing further analysis on the results and some extra measurements especially regarding pros and cons of LPR versus ER and ZRA versus EN.

Subproject 4 Development of electrochemical measurement system for corrosion rate measuring in district heating systems

Responsible: Olof Forsen, HUT
Co-workers: Antero Pehkonen, Jari Aromaa, Jaakko Leino, HUT
Kari Kärkkäinen, Coresto Oy

Background

In this research a reliable, compact and low-cost equipment for monitoring corrosion rates both inside and later also outside of district heating pipelines is under development. Field tests have been carried out in two locations in the district heating system of city of Mikkeli located about 250 km northeast from Helsinki, with some 38.000 inhabitants.

Also experiments in laboratory have been done. The aim of the laboratory test is to compare the equipment used in field tests to accurate laboratory potentiostats.

Most (80%) of the buildings in the city of Mikkeli are connected to the district heating system owned by Etelä-Savon Energia Oy. The annual heat production is about 350 GWh, of which about 99% is produced by the Pursiala power plant. Over 99% of the heat production in the power plant is based on wood and peat.

Activities

Field tests were done in the district heating pipeline. The outlet temperature of the district heating water in the power plant varies from 70 – 80°C in summer time and up to 120°C in cold winter periods. The inlet temperature is 45 - 50°C and maximum pressure 13 bar. The treatment of the tap water for district heating system consists of water softening and adding oxygen scavenger. Advantage-K-550 (Ashland) inhibitor is utilized 50-100 ml/m³ into softened water (0.1 – 1.0 ml/m³ surplus) to reduce the dissolved oxygen concentration and increasing the pH value of the water. A typical chemical composition of the district heating water is shown in table 4.4.1.

Table 4.4.1. A typical chemical composition of the district heating water.

pH	k / μ S/cm	hardness / °dH	Advantage-K-550 / mg/kg	Fe / mg/kg	Cu / mg/kg
9.17	272.50	0.36	0.30	<0.1	<0.02

Field tests were done in two locations: on 300 m from the power station (Pursiala) and the other in the farthest position of the pipe line system about 10 km from the power plant (Rantakylä). Electrochemical measurements were done using LPR and ZRA methods. Measurements have been carried out by two electrode coupling, where the pipeline is counter and reference electrode. The corrosion probe used in the field measurements, is shown in Fig. 4.4.1. The tip of the probe is carbon steel and the cylinder part isolated from the tip is copper. In this way measurements can be done both for steel and copper. The probe has also been used as zero resistance ammeter to monitor galvanic corrosion rates. The probes were installed directly to the pipeline (Fig. 4.4.2).

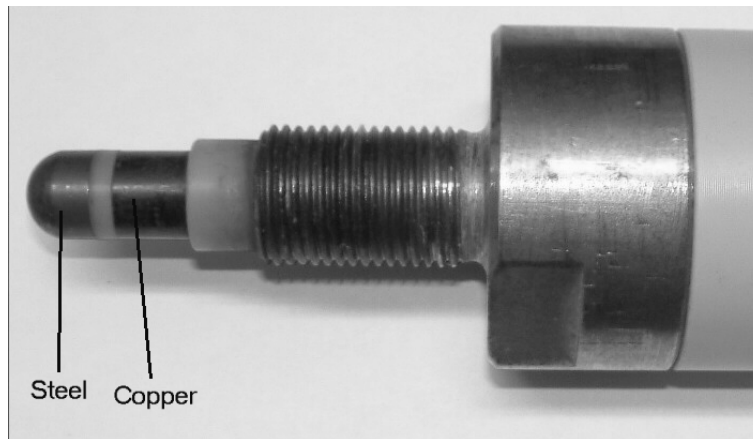


Fig. 4.4.1. Corrosion probe used in field measurements.

In Pursiala ZRA method was used. Measurements were carried out using a GPE-analogical measurement card, developed by Coresto Oy. The data amplified by the card was collected with a data logger. The measurement range of the card was $\pm 100 \mu\text{A}$, which has been converted to $\pm 10 \text{ V}$ output data. This means e.g. that $+10 \mu\text{A}$ is 1 V at the output. The data has been collected with a TinytagPlus data logger. The measurement range of the logger was adjusted to $0 - 10 \text{ V}$ and its resolution was 8 bit. The resolution of the instrument was 39 mV . This connected to the preceding measurement card gives the accuracy of about $0.4 \mu\text{A}$.



Fig. 4.4.2. The probe installation in Rantakylä.

In Rantakylä both LPR and ZRA methods were used. ZRA measurements were done using same type of GPE-analogical measurement card as in Pursiala. Data was collected by a Grant data logger serie 1000 where the measurement range was adjusted to 0 - 2V and the resolution was 16 bit. The measurement range of the card was $\pm 100 \mu\text{A}$, which has been converted to $\pm 10 \text{ V}$ output data. LPR measurements were carried out by MECO2000GSM measurement equipment, developed by Coresto Oy. The equipment was controlled by a programmable logic controller. Measurement data is automatically transferred by GSM SMS data transfer. MECO2000GSM unit sends the data automatically once a day to the data collection centre of Coresto Oy in city of Savonlinna about 100 km northeast from city of Mikkeli. On-line measurement data can be collected also by a GSM mobile phone. The parameters of the LPR measurements may also be changed using a mobile phone. In the measurement equipment a LCD screen exists for local monitoring and for adjustment of the parameters. The principle of the test equipment system is shown in Fig. 4.4.3.



Fig. 4.4.3. The principle of the test system.

Maximum of six potentiostatic polarisation steps for one test sample or one polarisation step for six samples can be done by the LPR measurement unit. The equipment may also be used in a potentiostatic mode. Measurements have been carried out so that four polarisations (–50, +50, -100, +100 mV) have been made for the steel sample and two (-100 and +100 mV) for the copper sample. The equipment will store the measured current values corresponding the polarisation potentials and counts the daily average of polarization resistance. So far experiments have been done in order to test the measurement equipment by maximal load.

The measurement range of the potentiostat is $\pm 1000 \mu\text{A}$, which is in output $\pm 10 \text{ V}$. The current is measured by a 12 bit converter (internal resistance $2 \text{ M}\Omega$) with a galvanic isolator. The $\pm 10 \text{ V}$ data is converted to 0 - 10 V range, and then 5 V corresponds zero current. The accuracy of measurement in potential is thus $1000 \text{ mV} / 4095 = 2.4 \text{ mV}$ and in the current $\pm 1000 \mu\text{A}$ or $1000 / 2048 = 0.48 \mu\text{A}$.

In LPR measurements the open circuit potential was measured before polarisation. Working electrode is polarised from the corrosion potential to a certain potential adjusted and the potential is hold at this potential for a certain time. Next polarisation is done after a time gap. In Rantakylä the parameters are at the moment: holding time 10 s, the gap between polarisation steps 30 s. Polarisation of -50 mV is done for 10 s and after 30 s the corrosion potential is again measured. Similarly polarisation of +50 mV, -100 mV and +100 mV is carried out.

Laboratory experiments

LPR and Tafel measurements were made in water from the district heating system in Mikkeli. Measurements were carried out at two temperatures (20 and 80°C). Nitrogen purging was used. As test materials steel and copper were used. The measurement range was $\pm 15 \text{ mV}$ from corrosion potential. The corrosion cell (15 ml) used is shown in Fig. 4.4.4.

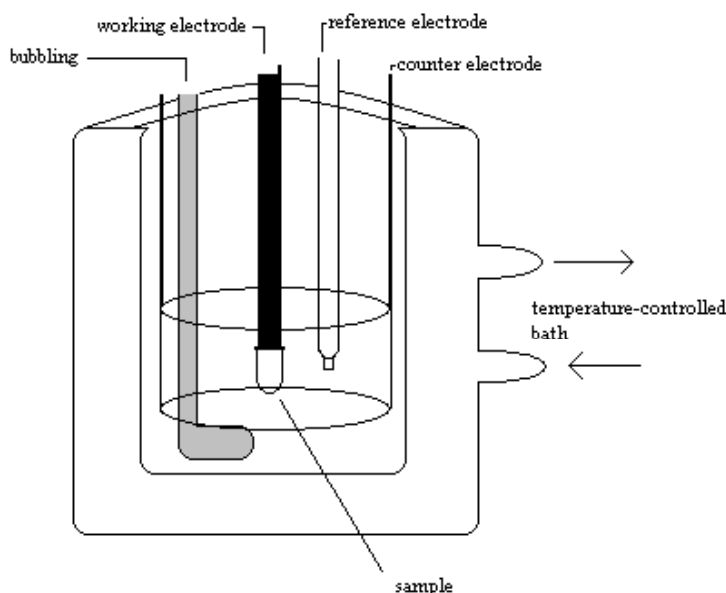


Fig.4.4.4. Schematic picture of the laboratory measurement cell.

Before experiments specimens were wet-ground to 600 grit, rinsed in distilled water and ethanol and dried up in hot air. The specimen was placed into the cell filled up with electrolyte, preheated if necessary. The specimen was stabilized for 30 min before the measurement was started. The counter electrode was an open cylinder shaped platinum electrode. Working electrode was almost similar to that used in the field measurements, except measuring one metal at a time. Reference electrode was Ag-Ag/Cl-electrode, Radiometer REF201.

Results

Field tests were done in the district heating system of city Mikkeli using ZRA and LPR methods from December 2001 to December 2003. In laboratory experiments the effect of inhibitor was investigated and the corrosion rate measured in laboratory and in field environments were compared.

3.1 Field tests

The measurements in Pursiala were done in the district heating pipe line about 300 m from the power plant. In Fig. 4.4.5 ZRA results between 18.12.2001 – 31.12.2002 are shown and in Fig. 4.4.6 results in 2003, respectively.

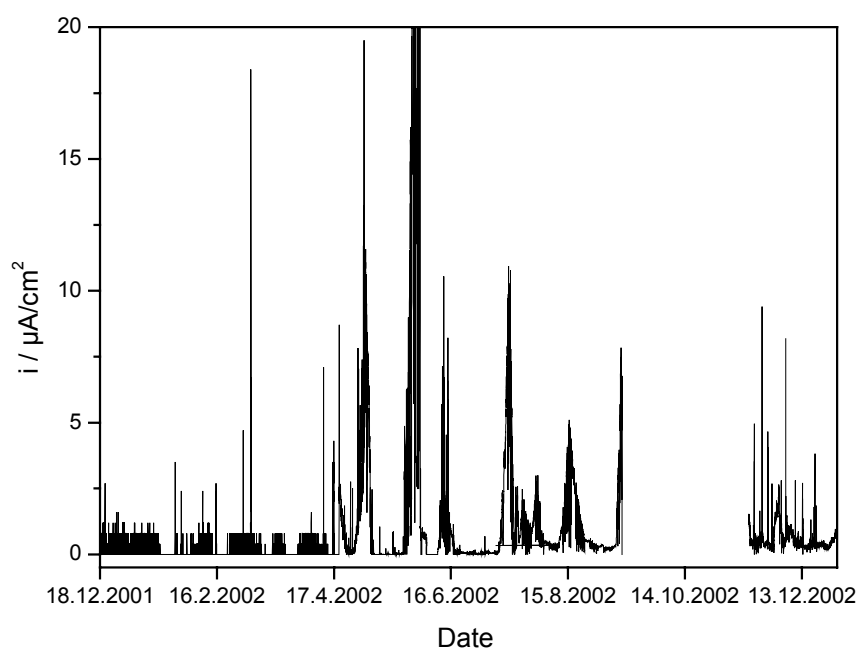


Fig. 4.4.5. Results of ZRA measurements during 18.12. 2001. – 31.12.2002 in Pursiala.

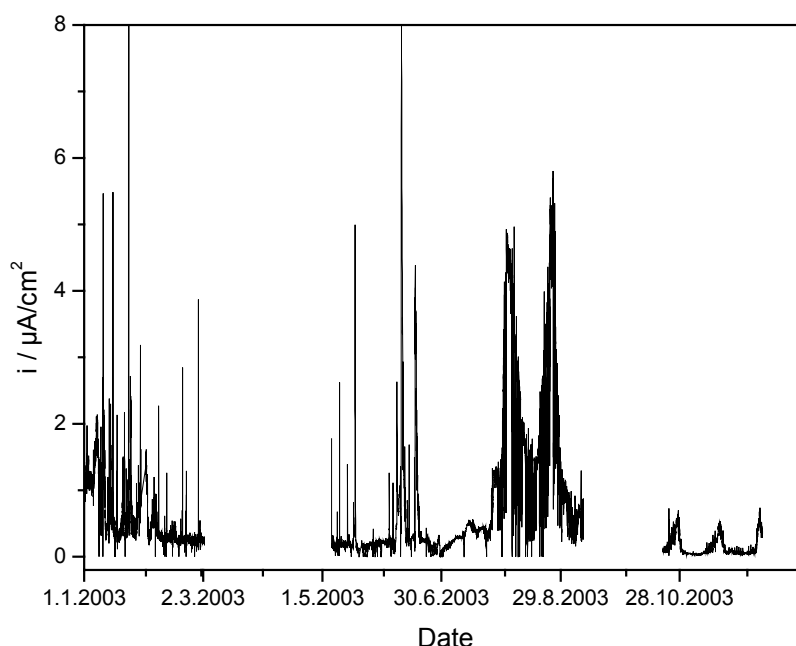


Fig. 4.4.6. Results of ZRA measurements during 1.1. 2003. – 31.12.2003 in Pursiala.

In Fig. 4.4.7 typical results of ZRA measurements during a shorter period of 4.5 months are shown. Current densities measured are mostly low, but some higher values may be seen for short periods. On 5th March higher values in ZRA measurements were found. The reason for the increased corrosion rates during the period is increased fresh water addition to the district heating system. During the period, 2.3. - 5.3 the water addition was three times higher (31.5 m³/day) than on average (12.3 m³/day). In Fig. 4.4.8 closer ZRA results and water addition during 28.2. - 7.3. is shown. This water addition has been so high that oxygen scavenger chemical was not able to remove the excess dissolved oxygen but after a few days delay. The chemical addition has also a certain delay after water addition.

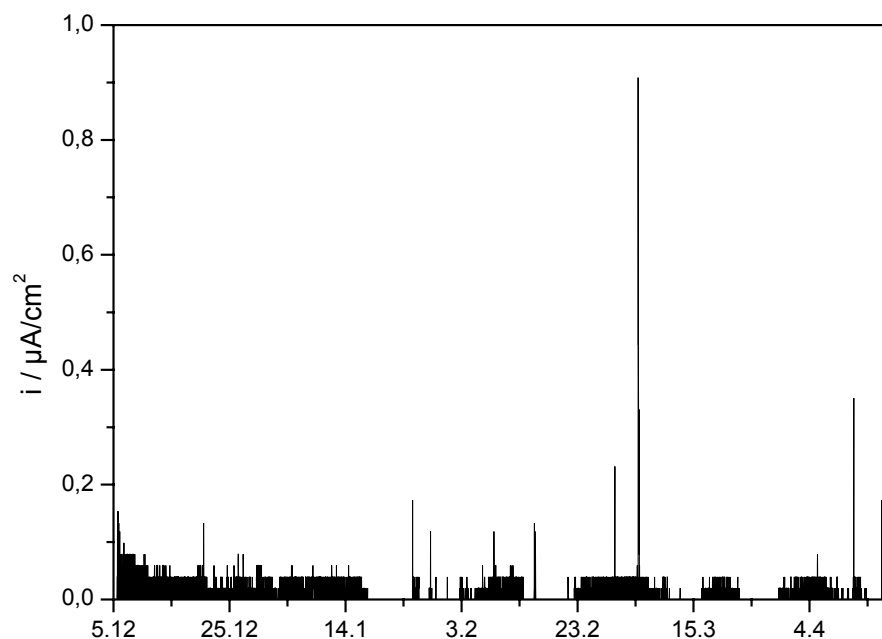


Fig. 4.4.7. Results of ZRA measurements during 3.12. 2001. – 18.4. 2002 in Pursiala.

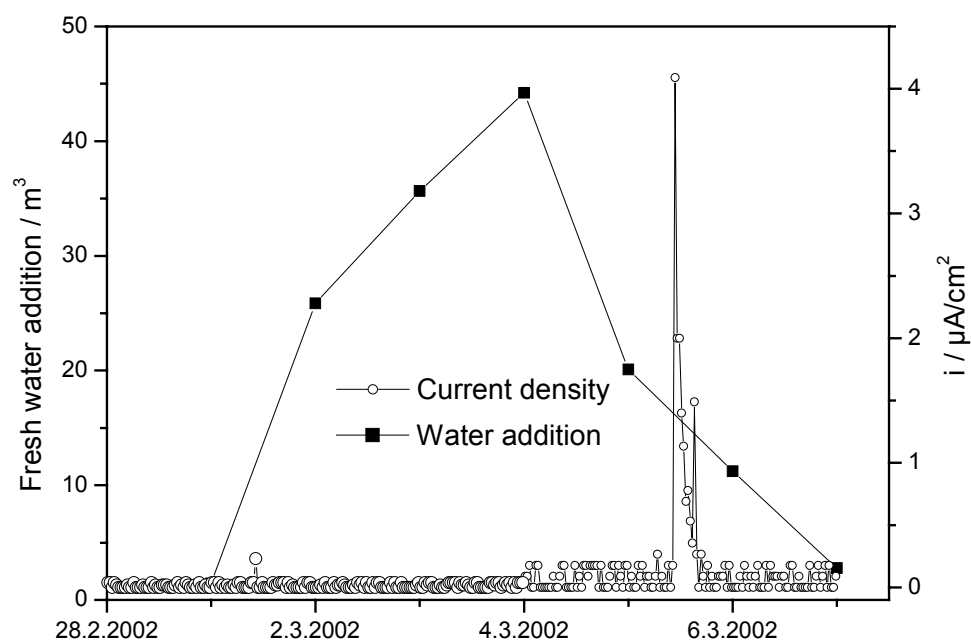


Fig. 4.4.8. Results of ZRA measurements and fresh water addition 4.3. – 7.3. 2002 in Pursiala.

Results of ZRA measurements during 5.12.2001 – 21.2. 2002 in Rantakylä are shown in Fig. 4.4.9. During 21.1. - 24.1. four small auxiliary boilers have been used because of a sudden shutdown in the power plant. When these boilers are taken to use, a low pressure may form in the system. In addition, it is possible that some water has been added, however no large amounts. The oxygen concentration increases also due to the quick lowering of the water temperature. These events may be seen in the ZRA results.

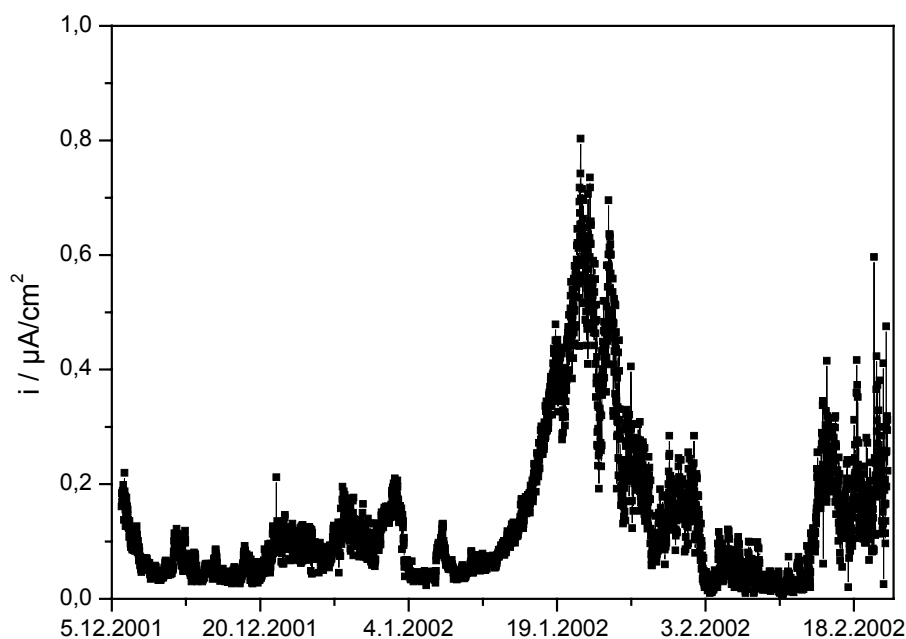


Fig. 4.4.9. Results of ZRA measurements 5.12. 2001 - 21.2. 2002 in Rantakylä.

In Fig. 4.4.10 results of ZRA-measurements between 29.6. – 31.10. 2003 are shown. High currents are due to lower inhibitor concentration and low water addition.

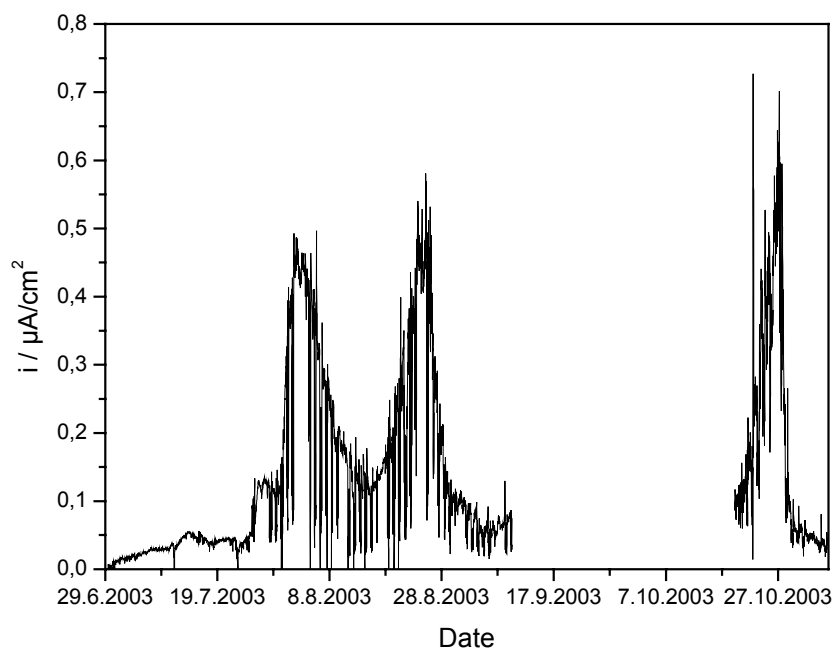


Fig. 4.4.10. Results of ZRA measurements 5.12. 2001 - 21.2. 2002 in Rantakylä.

In Rantakylä measurement site also LPR measurements were done. Corrosion potential of copper vs. pipeline before LPR polarisations are shown in Fig. 4.4.11. The behaviour of copper and steel electrodes is similar. Both react at the same time to the same direction. The changes in potential of copper are higher, which means that copper electrode is more sensitive to the changes in the corrosivity of the water. The reasons for all larger changes is not known, but periods of higher potentials 2. – 5.8. are somehow related to the shutdown during maintenance period, when it is possible that the pipelines are at least partly empty of water. The reason for lower potentials during 10. – 18.9. is obviously high water addition during 1. – 4.8. and also the periodically inhibitor addition (10 – 20 l). The previous inhibitor addition was done on 26.7. and the next after high water addition 8.8.

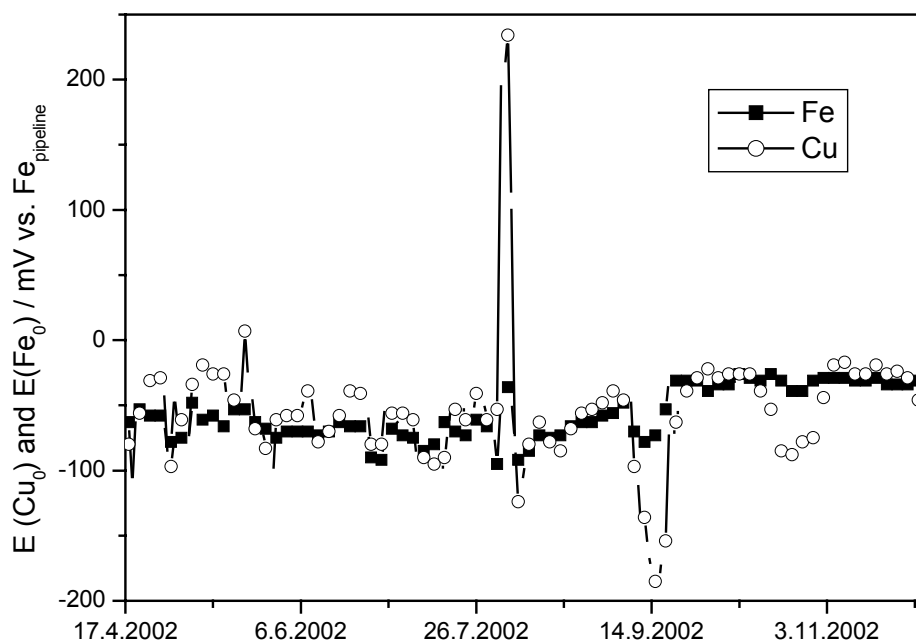


Fig. 4.4.11. Open circuit potentials of iron and copper before polarisation during in Rantakylä 2002.

From the LPR measurements corrosion rates of steel have been calculated using 40 mV/decade as a Tafel coefficient. Calculations have been done without IR-compensation. This preliminary value, which will be measured later more closely, has been measured in laboratory at 80°C using inhibited water taken from the district heating system in Mikkeli. This value is not an exact and correct value, because it should be measured by Tafel measurements in the district heating system, which is at the moment not possible. However, the exact Tafel coefficient is not so relevant because the exact corrosion rate is always difficult to measure, especially in systems like district heating pipelines, where corrosion rates are mainly very low and the corrosion mostly more or less local. The main issue in these measurements is to detect the changes in electrochemical factors as e.g. corrosion rates.

The corrosion rate of mild steel according to the LPR measurements in Rantakylä is shown in Fig. 4.4.12. No larger changes in the corrosion rate were seen. Corrosion rate values measured are at the level expected.

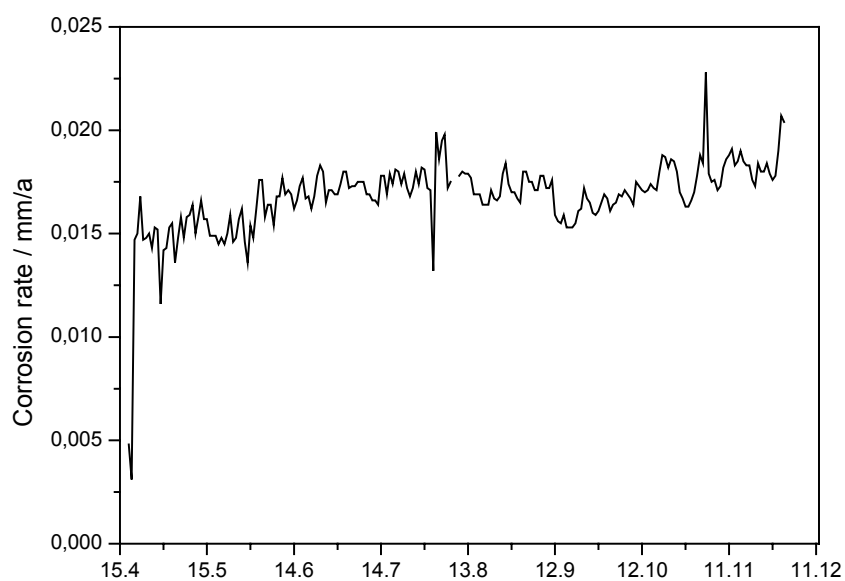


Fig. 4.4.12. Corrosion rate of mild steel in Rantakylä 2002.

Laboratory experiments

Results of LPR experiments for carbon steel measured in inhibited water from Mikkeli district heating system without gas purging at temperature 20°C made using PARC and ACM potentiostat, are almost similar (Fig. 4.4.13). The difference in the current densities measured by ACM and PARC potentiostat is minor.

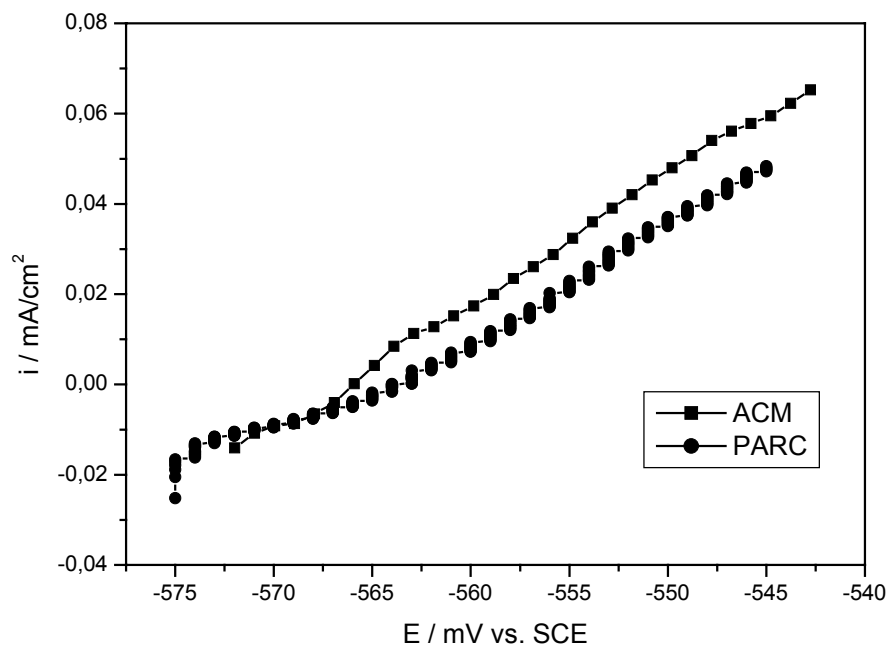


Fig. 4.4.13. Results of LPR-measurements using ACM and Parc potentiostat for carbon steel in inhibited district heating water from Mikkeli at temperature of 20°C.

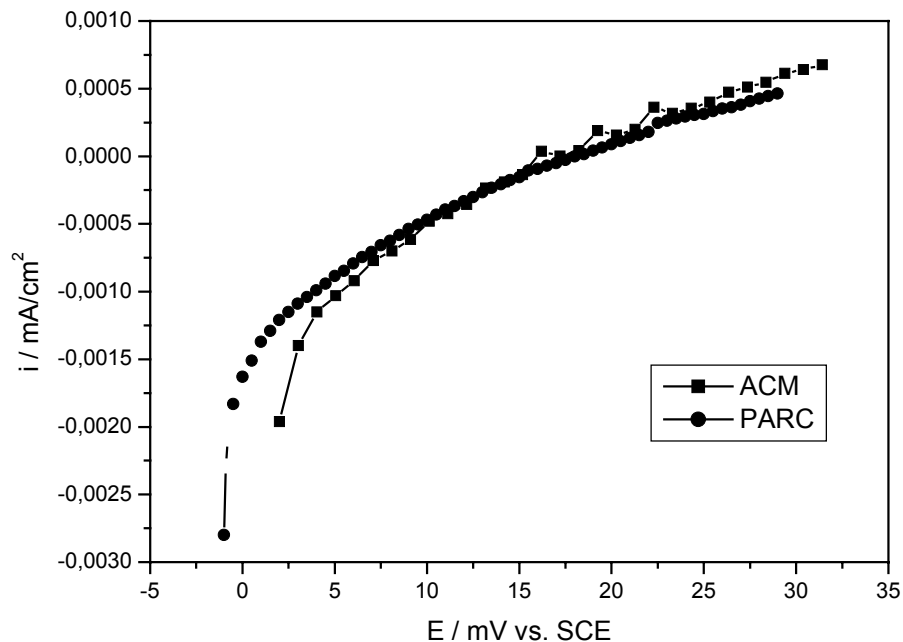


Fig. 4.4.14. Results of LPR measurements using ACM and Parc potentiostat for copper in inhibited district heating water from Mikkeli at temperature of 20°C.

Results of LPR measurements for copper carried out using ACM and Parc potentiostat are also close to each other (Fig. 4.4.14).

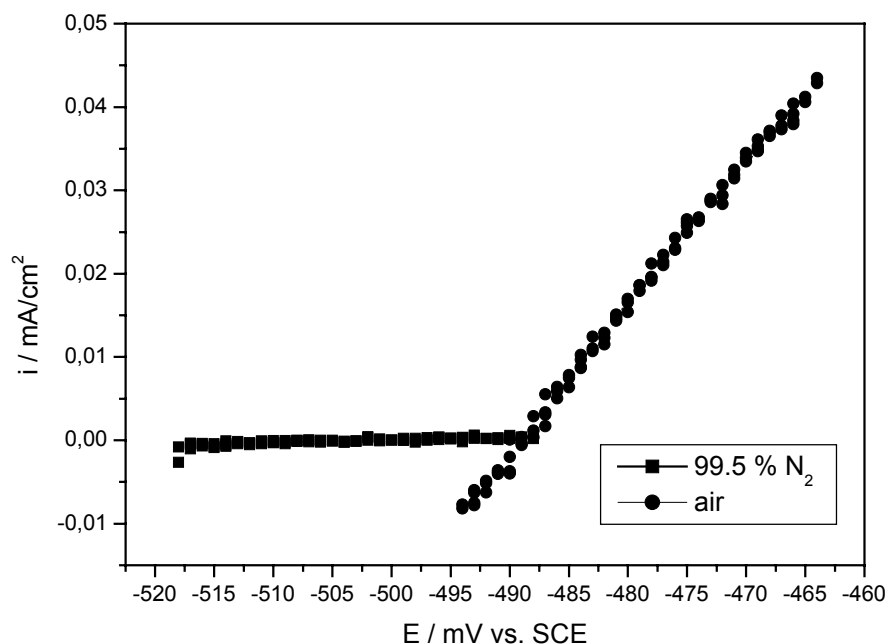


Fig. 4.4.15. The effect of N₂ and air on the LPR of carbon steel in inhibited water from Mikkeli at temperature of 20°C.

The effect of dissolved oxygen on the corrosion rate of carbon steel is large. The corrosion of steel is extremely dependent on the dissolved oxygen concentration of the water. This can be seen in Fig. 4.4.15, where results of nitrogen and air bubbling on the corrosion behaviour of carbon steel at temperature of 20°C is shown. Measurements have been done in inhibited water from Mikkeli. Results are median results of several repeated experiments carried out using both PARC and ACM potentiostats. There were no differences between PARC and ACM.

The Tafel plots for copper and carbon steel at temperature of 80°C without inhibitor and with nitrogen bubbling are shown in Fig. 4.4.16. The current densities have been calculated as an average current density of anodic and cathodic curve at corrosion potential. The current densities are 1.2×10^{-2} mA/cm² for Cu and 0.5 mA/cm² for Fe, respectively.

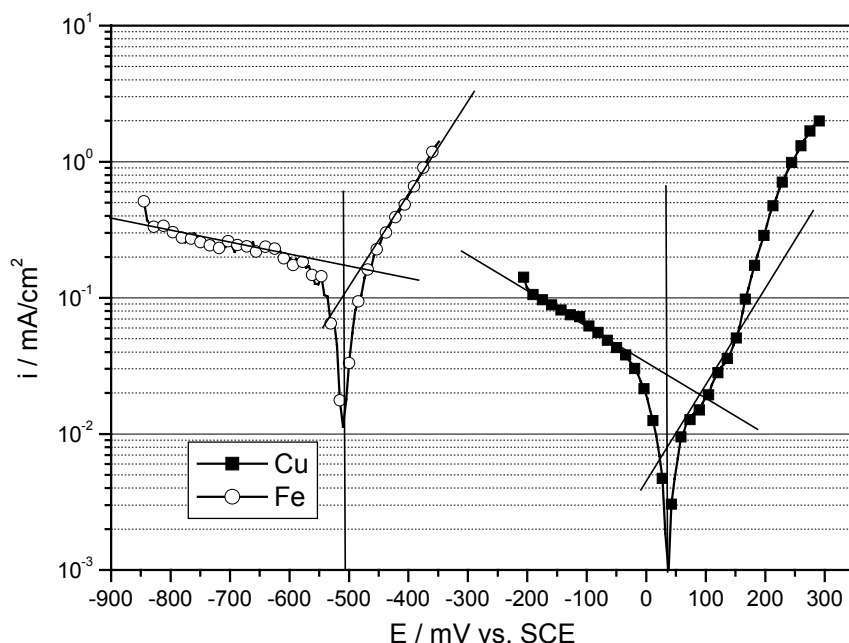


Fig. 4.4.16. Results of Tafel experiments for Fe and Cu in district heating water at temperature of 80°C.

The effect of the inhibitor (Advantage®-K550) used in the district heating system in Mikkeli was also investigated. The inhibitor is dosed straight into the district heating system and doses were between 50-100 ml/m³ in salt free water. If the water is taken through the gas removal dose should be 5-10 ml/m³. An overdose of about 0.1 – 1.0 ml/m³ should maintain in the system. In Fig. 4.4.17 the effect of inhibitor in tap water on the Tafel results of Cu is shown. Current density decreases as the inhibitor concentration increases. If the current density of Cu in pure water (Fig. 4.4.16) and in water with inhibitor addition (Fig. 4.4.17) are compared, it can be said that the effect of inhibitor on the corrosion rate of copper is slight.

The effect of inhibitor on the current density in Tafel plots of Fe are shown in Fig. 4.4.18. As the inhibitor concentrations increases, the corrosion potential increases also. The effect of inhibitor in the cathodic polarisation is small, but on anodic polarisation large.

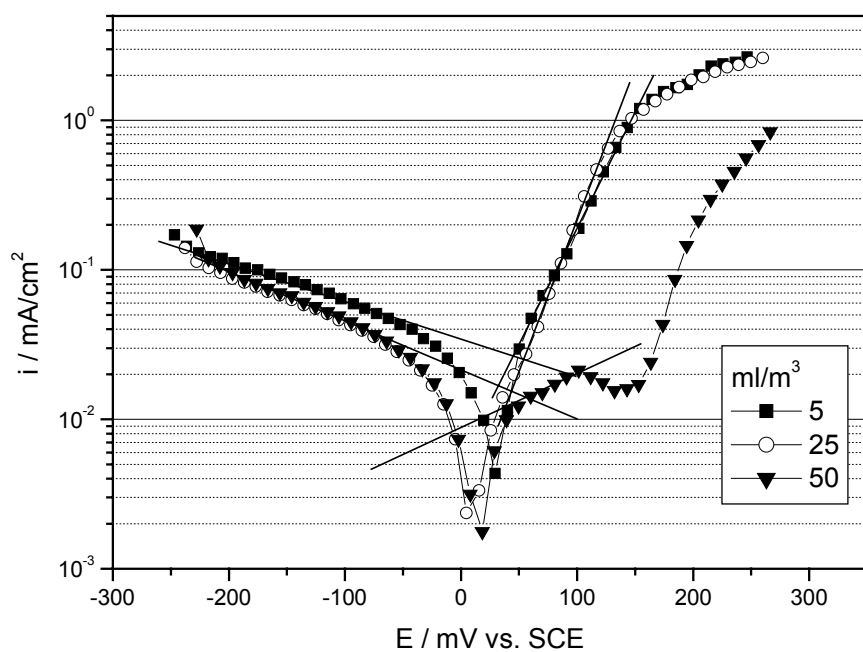


Fig. 4.4.17. The effect of inhibitor on copper in district heating water at temperature 80°C.

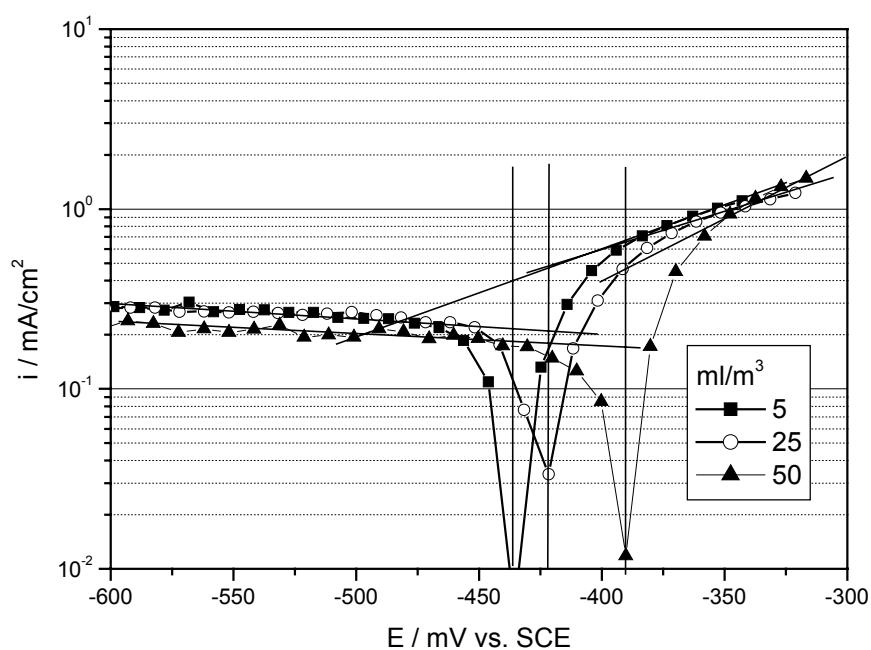


Fig. 4.4.18. The effect of inhibitor on carbon steel in district heating water at temperature of 20°C.

Conclusion

The measurement equipment, both ZRA and LPR method, seems to be suitable for continuous corrosion control in district heating pipelines. It has been found out that the measurement system and equipment as well the algorithm to calculate the polarisation resistance functions properly.

Both measurement methods (ZRA and LPR) seem to be able to monitor minor changes, e.g. an increase in oxygen concentrations due to water additions, on the corrosivity of the water.

The measurement equipment developed in this research with data transfer and remote control is a reliable low-cost system for corrosion control of low corrosion rates and changes in the corrosivity of the water in district heating systems.

Subproject 5 Measurement and comparison of microbiological activity and corrosion rate

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Background

The presence of micro-organisms in district water can on the inner surface of water-pipes form coatings, consisting of polymers secreted by the micro-organisms. These coatings, so-called biofilms, is a protecting environment for the micro-organisms, and the micro-organisms can in the biofilm form an environment that considerably diverse from the water environment outside the biofilm. The conditions in the biofilm can as time goes on be very corrosive for the material of the water-pipe, and corrosion in the form of pitting corrosion can occur. Corrosion influenced by the presence of micro-organisms is called microbiologically influenced corrosion (MIC), and if a biofilm has been formed, it can be very difficult to get rid of it.

High temperatures and water of high purity have a restraining influence on the presence of micro-organisms. Even under such circumstances though, MIC in district heating nets has been reported from the Nordic countries, and then in some cases even as penetrating corrosion. Even if more serious damages caused by MIC have not been reported in the Swedish district heating nets, there is still a reason to investigate the Swedish district heating nets regarding the presence of micro-organisms. One reason for this is that corrosion damages caused by MIC sometimes is not recognised as MIC due to unfamiliarity with the concept- with the result of not taking adequate measures. Another reason is that a biofilm can be formed without causing recognisable corrosion damages, while on the same time if formed on a heat exchanger reduce the capacity of the heat exchanger considerably.

The knowledge on how different water parameters influence the biofilm formation and MIC would result in guiding principles of the water quality of the district heating nets, minimising the micro-organism related problems. Parameters that influence the increase of micro-organisms in a district heating net are beside e.g. pH and the concentration of different species also the temperature of the water, wherefore also district cooling nets are of interest to investigate. One purpose of this sub project is therefore to study a number of district heating and district cooling nets regarding the biofilm formation and MIC, and relate this to the characteristics of the water of the different district nets. One way of doing this, and which is done in this project, is to expose samples to the water of the district nets. After a while the samples will be analysed regarding the presence of biofilm, the presence of micro-organisms in the biofilm, visual investigation of the corrosion and weight loss measurements.

An insufficiency with estimation of the corrosion rate using weight loss measurements is that the exposure time needed to receive a measurable result is quite long. Therefore there is a risk that the parameters that influence the amount of micro-organisms and the MIC will change during the exposure time, and thereby making it more difficult to estimate the dependence on the parameters.

A technique that in a short time can make an estimation of the corrosion rate would therefore be of great use. It would also be possible for the owner of the district net to utilise this technique, receiving a warning if the characteristic of the water changes in an unwanted direction. The so-called electrical resistance technique utilises the condition that the resistance in a metal changes when it corrodes. For the technique being available up to now, the resolution has not fulfilled the demands. However, MetriCorr, members of this project (see sub projects 2 and 3), has recently developed an instrument for electrical resistance measurements, having a resolution satisfying the demands.

Activities

General procedure

In this project so called exposure containers have been used, which are containers in where coupons can be placed, and through which district water can flow. The biofilm formed on the coupons and the corrosion on the coupons can thereafter be investigated. This results in an understanding of the conditions for the inner surfaces of the tubes of the district cooling net. The project was separated in two parts. Phase 1 has mainly consisted of estimating whether microbial presence can be found in a district net, and, if so, to what degree. Phase 2 has partly consisted of estimating the potential of corrosion and microbial activity for different district water qualities, and partly by trying to get a picture of the growth of micro-organisms over a longer period.

The exposure containers were connected to the district nets, letting the district water go to waste after passing through. All the district nets were located in Stockholm, and one exposure container was connected to each net. For phase 1 two district cooling nets were investigated, located in the region of Värtan (A) and Hammarby (B). For phase 2, these two nets were investigated again, but also two district cooling nets located in Solna (C) and Huddinge (D), and two district heating nets located in Hässelby (E) and Värtan (F). For phase 1 the exposure containers were connected from the end of June 2001 to the middle of August the same year, while for phase 2 from the turn of the month May/June 2002 to the middle of June 2003. The removal of the coupons for phase 2 took place at three occasions; October 2002, March 2003 and June 2003. Examples of connection for two of the nets can be seen in Fig. 4.5.1.



Fig. 4.5.1. Exposure container used during phase 1.

Equipment

For phase 1 an exposure container made of stainless steel was used. It was formed as a cylinder with a length of about $\frac{1}{2}$ m and a diameter of about 1 dm (see Fig. 4.5.2a). The coupons were plates of carbon steel with the dimensions 2 x 3 cm. The coupons were connected with a plastic screw to a small rod, which in turn was connected to a threaded block (see Fig. 4.5.2b). The blocks with their coupons were connected to the exposure container by screwing them through holes in the exposure container. To avoid electrical contact between the coupon and the rod of the block, a plastic spacer was placed between the coupon and the rod, and a plastic screw was used. Just before the inflow to the exposure container, a valve and a flow meter were connected, for enabling checking and regulation of the flow.

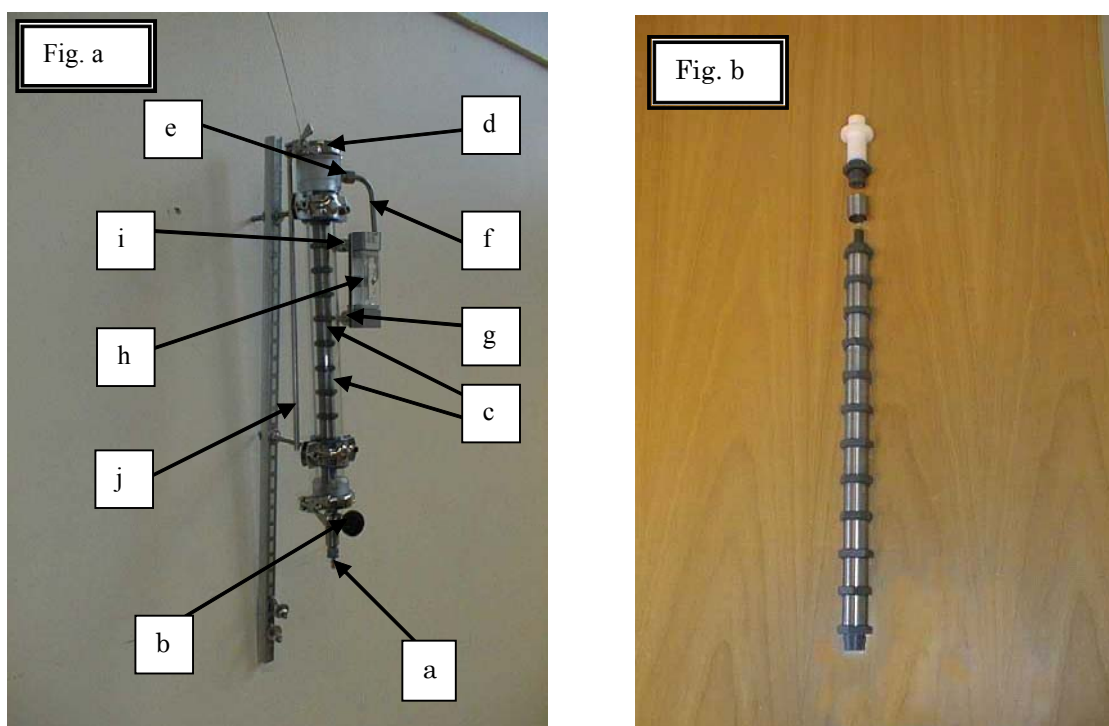


Fig. 4.5.2. Exposure container phase 2. Fig. a, exposure container with belonging units: a) inlet from district net, b) regulator for flow, c) coupons (sitting on separable plastic units), d) opening for successive withdrawal of coupons, e) outlet from exposure container to flow meter, f) connection 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. Fig. b, 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.

For phase 2 another and a bit more sophisticated exposure container was used compare to the one used in phase 1. The exposure container of phase 2 is with smaller changes still used by the Swedish Corrosion Institute when analysing the conditions for microbial activity and corrosion of a district net. The main part of this exposure container consists of a cylinder of PVC plastic, with the length of $\frac{1}{2}$ m, and with a diameter of $\frac{1}{2}$ dm (see Fig. 4.5.3a). 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 (Fig. 4.5.3b). 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, just so much that only the coupons that shall be withdrawn are exposed to air. Then these coupons are withdrawn, the empty plastic peace 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). The difference between the exposure cylinder used during phase two and the one now used by the Swedish Corrosion Institute, is that the cylinder then used was made of polycarbonate.



Fig. 4.5.3. Examples of locations for connection of exposure containers. The picture to the left is from the net at Värtan and the other picture is from the net at Solna. The exposure containers are covered with a foam plastic case for avoiding possible interference from surrounding light. Beside the exposure containers is a notebook for regularly notifications of the temperature and the flow of the district cooling water.

Samples and sample handling

The coupon material for both phases was seamless carbon steel. For phase 1 the samples were flat and rectangular, with the surface dimension 2 x 3 cm and thickness 2 mm. For phase 2 the coupons were formed as cylinders with the dimensions height 2.5 cm, inner diameter 1.9 cm and outer diameter 2.2 cm. For both phases the coupons before the exposure were pickled, rinsed in ethanol and air-dried. For phase two the coupons also were weighed.

The plastic bottles which were used during sampling were sterilised the same day as the sampling, rinsed with ethanol and filled with 50 ml of sterilised water (municipal water sterilised in pressure-cooker at 125°C during 15 minutes). At every sampling occasion three coupons were withdrawn, and a water sample was taken. The sampling was made following normal sterilised routines. The coupons were placed in separate bottles and the water was allowed to pour a short while before a water sample was taken. The sample treatment was either made directly after sampling or at maximum after a week, while the samples were stored in a fridge. To loose the biofilm the bottles with the coupons were placed in a UV-bath for 10 minutes and thereafter shaken for an additional 5 minutes. The coupons were picked up from the bottle with a sterilised tweezers, rinsed in ethanol and dried by a burner flame. In phase 2 the coupons also were weighed. Finally the coupons were investigated optically. The bottles with the water sample and the bottles with the loosened biofilm were investigated using microbial techniques (see Microbial analyses).

Microbial analyses

General

In this project the determination of present micro-organisms has 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 micro-organisms, and both dead and viable). The determinations were made both for the district water and for the biofilm. The groups of viable micro-organisms which were determined were the group of aerobic heterotrophic bacteria, the group of sulphate reducing bacteria (SRB), and the group of fungi. The district water and the solutions with loosened biofilm were exposed to a nutrient of a certain kind for each group of micro-organisms. The nutrient media for aerobic heterotrophic bacteria were named nutrient agar (NA) and plate count agar (PCA), while for fungi malt extract agar (MA). For these two groups agar gel was used as the nutrient medium while for SRB a liquid medium was used. All the liquid preparations and the following handling were made following normal sterilised routines. For determination of the total amount no special solutions were used.

The risk for microbial related problems can to some degree of reliability be related to the concentration of micro-organisms in the district water and especially in the biofilm. For a *total concentration in the district water* of 10^3 - 10^4 per cm^3 of micro-organisms, it can be said that there are no alarming danger but that the reason for the relatively high level needs to be checked, 10^4 - 10^6 per cm^3 that there is something wrong with the system and above 10^6 per cm^3 that the level is alarmingly high. For a *total concentration in the biofilm*, a total concentration of micro-organisms less than 10^6 per cm^2 can be regarded as low, between 10^6 and 10^8 per cm^2 that a stable biofilm is about to form and above 10^8 per cm^2 that a fully covering and viable biofilm has been formed. For the *concentration of viable aerobic heterotrophic bacteria in the water*, 10^3 per cm^3 is regarded as a safety limit and 10^7 per cm^3 as an acceptable but somewhat risky level. For the *concentration of viable aerobic heterotrophic bacteria in the biofilm*, 10^7 per cm^2 is also regarded as an acceptable but somewhat risky level. Finally it has to be stressed that the mentioned limits are estimations,

partly received from general experiences. Therefore it is possible that the limits can differ between different nets, especially if the conditions are special.

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, 1 ml was withdrawn from the respective sample solution, i.e. the solution with biofilm or the sample with district water. This volume was added to a nutrient solution for SRB of 10 ml. 1 ml of the resulting mixture was then added to a second nutrient solution of 10 ml. Finally 1 ml of this mixture was added to a third nutrient solution, also 10 ml. For every sample solution three dilution series of this kind was made. If growth occurs the nutrient solution becomes black. The estimation of the number of SRB in the sample solution was made by after a certain time count the number of coloured nutrient solutions. Then this number was related to a table, specifically constructed for the purpose (see Microbiologically Influenced Corrosion. B J Little, F Mansfeld & P A Wagner. NACE International 1997). This gave the concentration of the sample solution, i.e. the concentration of the district water or in the biofilm solution. The latter then gave the concentration in the biofilm by utilising the value of the solution volume and the value of the exposed area of the coupon.

Agar gel growing micro-organisms

The method to determine the concentration of micro-organisms by cultivating on an agar gel means that the sample solution first is applied on a nutrient filled gel. The micro-organisms multiplies and after a while colonies are formed which can be seen as black dots on the gel. After about 10 days one assumes that the micro-organisms do not multiply any further and the black dots are counted. Ideally it is expected that all the micro-organisms are multiplied and each one forming an isolated colony seen as a black dot. Therefore the number of black dots ought to correspond to the original amount of micro-organisms on the gel. However, some micro-organisms does not multiply at all, and some are located so close to each other that the colonies formed are overlapping. Generally, it is assumed that the number of dots has to be multiplied by a conversion factor of 10.000 to give the original amount.

To estimate the concentration of viable agar gel growing micro-organisms, three volumes of 0.1 ml was taken from each sample solution. These three volumes were divided between three agar gel plates, having the nutrient solution MA, NA and PCA, respectively. After applying of sample solutions, growth of micro-organisms was awaited. The amount of micro-organisms in the applied volume was then given by counting the black spots on the gel. This in turn gave the concentration in the sample solution.

Total

The total amount of micro-organisms was estimated by using a small beaker, consisting of two joined glass plates. The intervening space was 0.1 mm, and one of the plates was 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 beaker, resulting in a filling of the intervening space due to the capillary force. The beaker was then placed in a microscope with 400 times magnification, followed by a counting of the micro-organisms. The concentration of the sample solution was calculated by utilising the known volume of the beaker.

Results

Phase 1

Plant A

The net of Plant A was initially filled with municipal water, which during phase 1 also was used as the feed water. Municipal water is neither degassed, deionised nor alkalised. After sampling it could be seen that biofilm had been formed over the whole surface of the coupons. Analyses of the presence of micro-organisms were made according to table 4.5.1.

Table 4.5.1. The result of analyses on the concentration of micro-organisms in different district waters and in biofilm on exposed coupons.

	District water (cm ⁻³)					Biofilm (cm ⁻²)				
	Total	Viable				Total	Viable			
		NA	PCA	MA	SRB		NA	PA	MA	SRB
A(E)	17·10 ⁶	14880	15840	10	210	140·10 ⁶	37000	20000	230	33
A(I)	9·10 ⁶	260	150	<10	2					
B(I)	<0.7·10 ⁶	46	34	<2	0.1					

Analyses were made for the nets of plant A and B (see Activities/ General procedure). For plant A, the analyses of the district water were made both for the inflow (I) and for the inside of the exposure container (E). The analyses were made partly on agar gels; nutrient agar (NA), plate count agar (PCA) and malt extract agar (MA), and partly in solutions; sulphate reducing bacteria, SRB. The values for the biofilms are mean values from three coupons.

It can be seen that the total concentration of micro-organisms of the district water in the exposure container is of an alarmingly level. This is also the case for the concentration of viable micro-organisms when taking the adjustment factor into account (see Microbial analyses/General), except for fungi (MA). For the district water outside the exposure container, only the value of the total concentration is of about the same level. For the biofilm the levels of viable micro-organisms (except for fungi) are also alarming and almost as much for the total concentration. When the degree of corrosion on the coupons was estimated, surface damages could clearly be seen.

Plant B

The net of Plant B was filled with water of district heating quality, and feed water used was also district heating quality. The water of district heating quality had both been degassed, deionised and alkalised. After sampling, it could be seen that except for the total concentration in the biofilm, the values were on an acceptable or lower level. When estimating the degree of corrosion on the coupons, surface damages were hardly noticeable.

Phase 2

Description of the district cooling nets

Specifications of the district water and the nets themselves for the district cooling nets of phase 2 can be seen in table 4.5.2 and 3, respectively. In table 4.5.3, two dates are given for net D, 1974 and 1999. This is explained by the fact that the district cooling net of region D was started in 1974, certainly as a smaller internal net, but has thereafter been built out to its present size, which was achieved in 1999.

Table 4.5.2. Analyses data for different district waters.

Net	Date (year, month)	Cond. μS/cm	pH	Hardness dH	Ca mg/l	Fluoride mg/l	Additives
A	0205-0306	121 (100, 149)	9.6 (9.7, 9.4)	1.9 (1.5, 2.5)	-	0.35 (0.32,0.38)	Pyranine
B	0205-0306	98 (87, 116)	9.8 (9.4, 9.9)	0.20 (0.08, 0.38)	-	0.36 (0.26,0.51)	Pyranine
C	0210, 0310	210, 220	9.0, 9.2	0.9, 1.6	-	-	NaOH
D	0201,0310	170, 180	8.9, 8.8	3.00, 2.98	-	-	-
E	0205-0306	18 (17,20)	9.8 (9.7,9.9)	-	0.19 (0.08,0.34)	0.05 (0.04,0.07)	Pyranine
F	0205-0306	45 (41,52)	9.7 (9.3,9.9)	-	0.46 (0.18, 0.96)	0.14 (0.08,0.35)	Pyranine

"Cond." stands for conductivity. For net A, B, E and F values for each month has been received, from which mean values are given with minimum and maximum values between brackets. For net C and D only values from two occasions have been received.

Table 4.5.3. Specifications of different district cooling nets.

Plant	Vol. m3	Base (opening year)	Feed (origin)		Feed (change)			Feed (turnover) share/y
			Degassed	Deionised	year	Degassed	Deionised	
A(DCW)	11000	Raw (-94)	No	No	2002	Yes	Yes	1/2
B(DCW)	4000	DH (-98)	Yes	Yes	-	Yes	Yes	1/2
C(DCW)	4500	Raw (-95)	No	No	2001	Yes	Softened	"Very small"
D(DCW)	400	Raw (-74,-99)	No	No	-	No	Nej	about 1 %
E(DHW)	15600	Raw (-51)	No	softened	70-ties	Yes	Yes	1
F(DHW)	32200	Raw (-61)	No	softened	70-ties	Yes	Yes	1

"Vol." stands for volume, "Base" for the water initially filling the net, "Feed" for feedwater, "DCW" for district cooling water, "DHW" for district heating water, "Raw" for municipal water, "DH" for water of district heating quality.

Microbial analyses

The results from the analyses of the total concentration can be seen in diagram 4.5.1, a-f. The axes of the diagrams have been given the same resolution for facilitating a quick visual comparison. Both regarding the total concentration in the biofilm (unbroken line) and in the district water (broken line), it can be seen that the values for the six district nets are mainly of about the same order. The largest deviation regarding the biofilm is for net E, the third sampling occasion. Regarding the district water, the largest values can be seen for net E, and for the first sampling occasion for net C and D.

The results of the analyses of viable micro-organisms can be seen in diagram 4.5.2, a-f. The axes of the diagrams have also here been given the same resolution for facilitating a quick visual comparison. The analyses on gel with MA were not made for sampling occasion 2, and the samples from net D, first sampling occasion, was damaged during the treatment and could not be utilised. One can see that the values for MA, i.e. concerning the group of fungi, both for the biofilm and the district water, are very low and hardly above the x-axis in the scale used. The opposite is for the NA and the PCA values, i.e. for the aerobic heterotrophic organisms. Therefore, the MA results will not be discussed further, and only referring to the aerobic heterotrophic organisms if nothing else said. One can also see that both the values of for the biofilms and for the district water vary more compared to the values in diagram 1. This is both when comparing within and between each net.

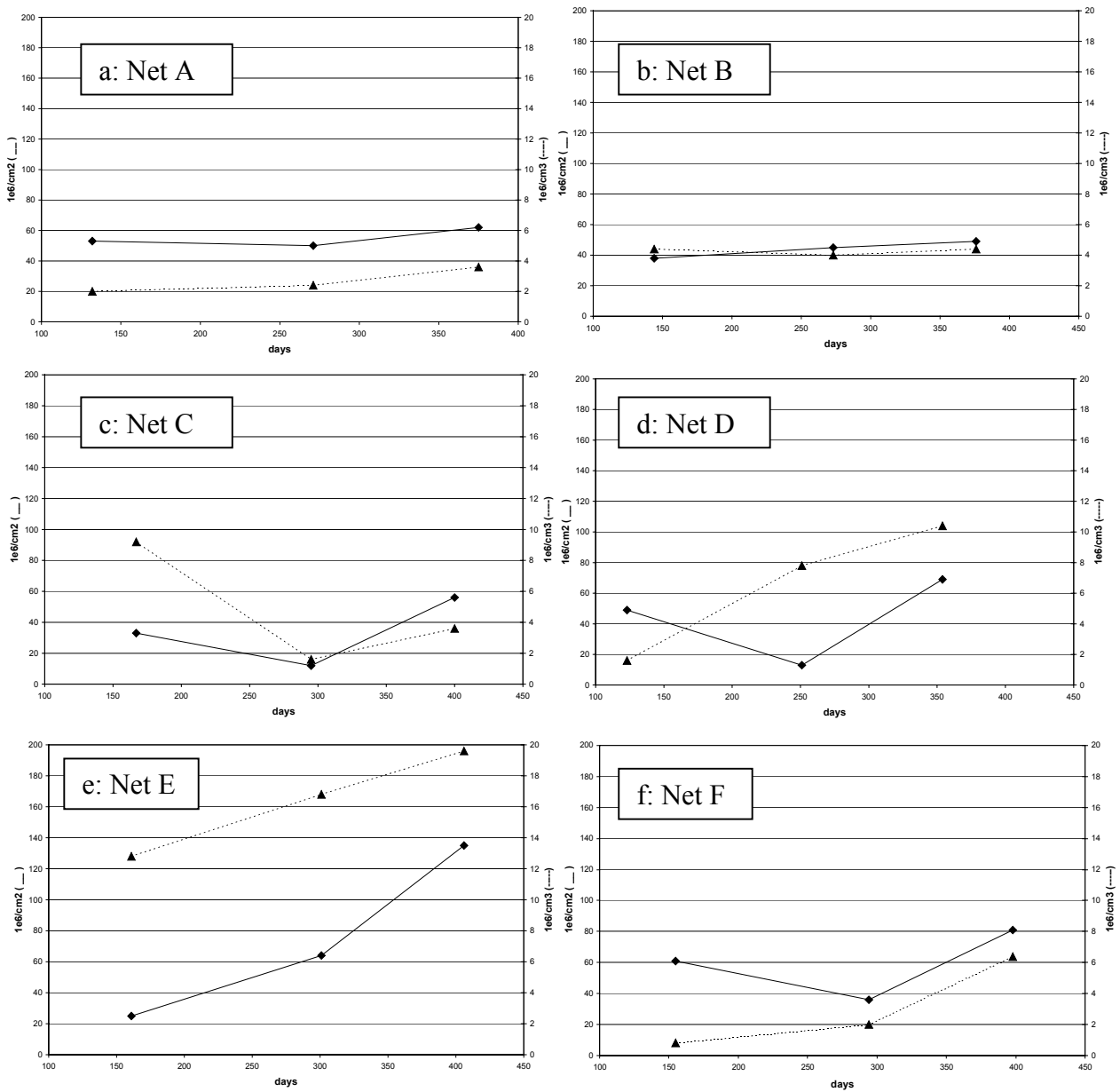


Diagram 4.5.1 a-f. Total concentration of micro-organisms. Squares with unbroken lines stand for biofilm and broken lines with triangles for district cooling water.

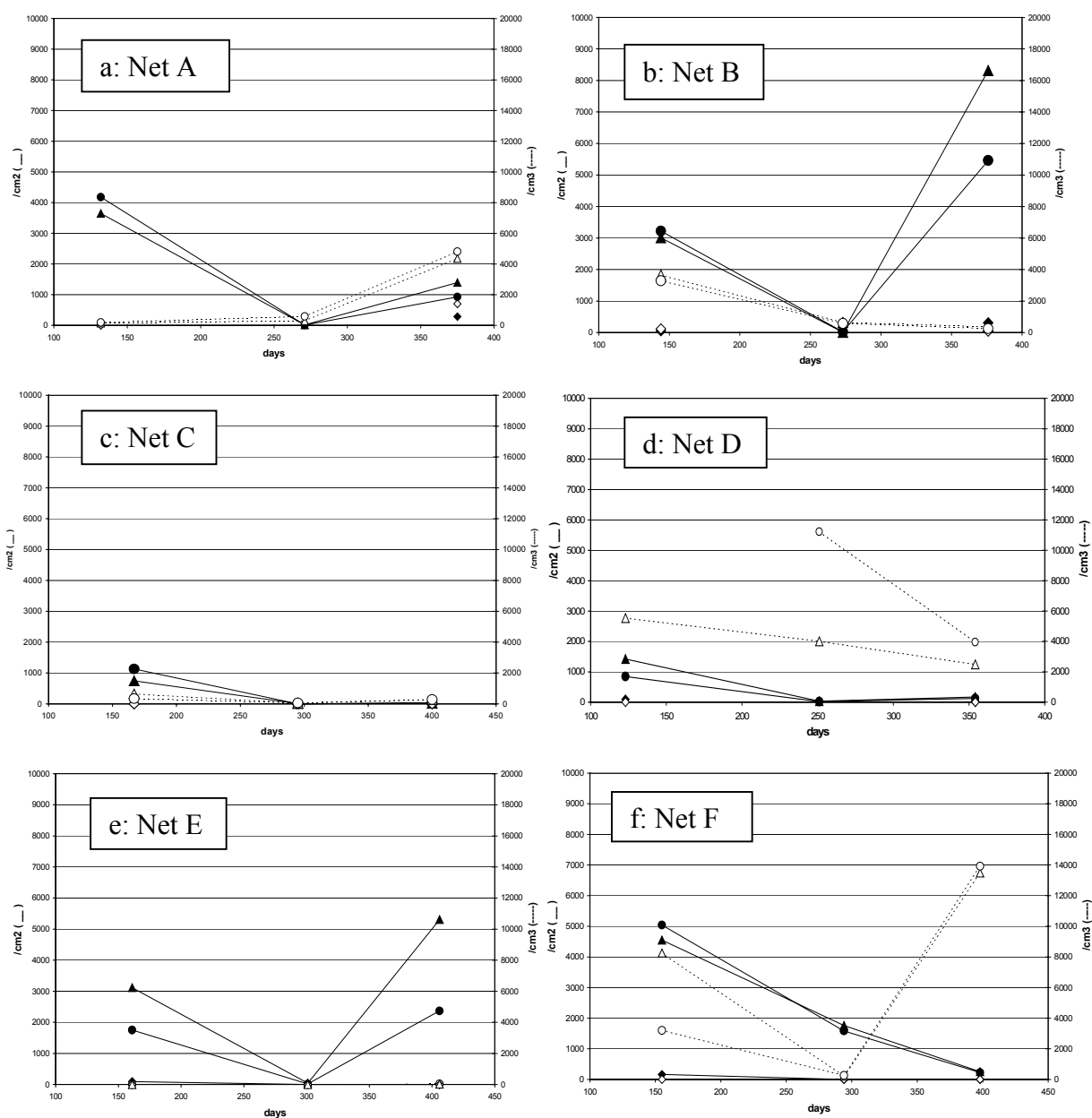


Diagram 4.5.2 a-d. Concentration of viable micro-organisms in district cooling nets, estimated by agar gel growth. Squares stand for malt extract agar (MA), triangles for nutrient agar (NA), and circles for plate count agar (PCA). Unbroken lines with filled markers stand for biofilm and broken lines with unfilled markers for process water.

For the biofilm the lowest values are generally from the second sampling, except for net F, where the values are decreasing from the first sampling occasion. For the district water no general trend can be seen. Worth noticing is that the concentration of micro-organisms in the district water has gone down at the third sampling occasion for plant B, while the opposite is the case for the biofilm.

Concerning SRB, only very small amounts have been found, 2 per litre, and then for plant D.

Corrosion attack

The corrosion rate was calculated from weight loss measurements on the coupons. It could be seen that for all sampling occasions and all district cooling nets the corrosion rate was fairly small, about 1-2 μm per year. No pitting corrosion could be seen.

Comparison between different district water qualities with respect to potential for microbial growth

The results from phase 1, table 1, shows that net A has a much higher concentration of viable micro-organisms than net B, both for the district water and the biofilm on the coupons. Since net A had a water quality without degassing and deionisation while net B had, this seems to show that degassed and deionised district water clearly reduce the potential for microbial growth. This is also supported by some of the results from phase 2. Net D has, according to table 3, district water of a low quality, neither degassed nor deionised, compared to net C, which has feed water which is degassed and softened, and especially compared to net A, B, E and F which has feed water that is degassed and deionised. This is in accordance with diagram 2, showing the values of the district water for net D, being among the largest.

The conclusion that degassed and deionised district water clearly reduce the potential for microbial growth is seemingly contradicted by the fact that the values for the district water of net D could be expected to differ more compared to the other nets. It can also be seen that the levels of viable micro-organisms in the biofilms for net D are at the same level as for net C and considerably lower than the other nets. A possible explanation to the higher concentration in net A, B, F and G could however be that pyranine here is added to the district water. Pyranine is added for the reason to easily detect a leakage, but is at the same time a carbon compound, and as such a nutrient for heterotrophic micro-organisms.

Risk potential for each net with respect to microbially related problems

The total concentration of micro-organisms in the district water has for all the nets been shown to be between 1 and 20 million per cm^3 , see diagram 1. This is to be compared with the general opinion, see Activities/Microbial analyses/General, that a total concentration in the district water above 1 million per cm^3 is regarded as high. Concerning the total concentration in the biofilms, these values have shown to be between 10 and 135 million per cm^2 . This is to be compared with the opinion that a stable biofilm is about to be formed if the concentration is between 1 million and a hundred million per cm^2 , and that a fully covering and vital biofilm is developed if the concentration exceeds 100 millions per cm^2 . The largest values for the district water and the biofilm can be seen for net E (diagram 1e), and then at the third sampling occasion. The values for both the district water and the biofilm have also continuously been increasing since the first sampling occasion. This makes net E to the net with the clearly highest risk potential. A more thoroughly investigation could here be recommended.

The concentration of aerobic heterotrophic bacteria for phase 2 in the biofilms and in the district water, estimated by using nutrient agar (NA) and plate count agar (PCA), is shown in diagram 2. The largest values for the biofilms and for the district water of each net are presented in table 4.5.4.

Table 4.5.4. Maximum values for concentration of aerobic heterotrophic bacteria.

	Net A		Net B		Net C		Net D		Net E		Net F	
	NA	PCA	NA	PCA	NA	PCA	NA	PCA	NA	PCA	NA	PCA
Biofilm + χ (/cm ²)	3647 36·10 ⁶	4176 42·10 ⁶	8314 83·10 ⁶	5461 55·10 ⁶	745 7·10 ⁶	1132 11·10 ⁶	1422 14·10 ⁶	848 8·10 ⁶	5309 53·10 ⁶	4745 47·10 ⁶	4549 45·10 ⁶	5044 50·10 ⁶
DW + χ (/cm ³)	4360 44·10 ⁶	4810 48·10 ⁶	3650 36·10 ⁶	3290 33·10 ⁶	640 6·10 ⁶	340 3·10 ⁶	5535 55·10 ⁶	5615 56·10 ⁶	20 0.2·10 ⁶	20 0.2·10 ⁶	13480 135·10 ⁶	13920 139·10 ⁶

Estimated by using nutrient agar (NA) and plate count agar (PCA). “ χ ” means conversion factor (see Activities/ Microbial analyses/ General) and “DW” means district water.

Here it can be said that for the biofilms, the maximum values for NA nad PCA for each net have been between round 1000 per cm² (net C), and slightly above 8000 and 5000 per cm³ respectively (plant B). With the adjustment factor of 10 000 (see Activities/ Microbial analyses/ General), values are received which are on a level with (net C and D) or above (net A, B, E and F) 10⁷ per cm², which is seen as an acceptable but somewhat risky level. For the district water, it can be said that the levels are much lower (net E), slightly lower (net C), above (net A, B and D) and much above (net F) 10⁷ per cm³, which can also be seen as an acceptable but somewhat risky level, even though all levels are much above the safety limit.

Variations in micro-organism concentration during the exposure period

The concentrations of aerobic heterotrophic bacteria, diagram 2, can be seen vary relatively much between the sampling occasions, especially for net A, B and E concerning the biofilm, and net F for the district water. These variations forms a minima, which also is the case for net C and D for the biofilm and net C for the district water, however only seen from the original data. A reasonable explanation for this variation is the water temperature. During wintertime the district cooling water, net A-D, is less utilised while the opposite situation is for the district heating water, net E and F. This results in a lowering of the temperature of the district cooling water and an increase of the temperature of the district heating water. This in turn results in temperatures close to zero and above 70 °C respectively. Usually optimum for the bacteria is between 30°C and 50°C. During wintertime, i.e. the second sampling, the temperature has been deviating from the optimum for a while, therefore resulting in a decrease in the bacteria concentration. For the concentration in district water for net B and D, and in the biofilm for net F, the concentration decreases from sampling 1 to 2, but also continues to decrease for sampling 3. A plausible explanation for this is that a longer recovering period sometimes is needed after a deviation from the optimum temperature.

Even if the feed water is kept on a high quality level, pollutants can be introduced to the district water by the connection of new customers. This occurs relatively often and has the result that new pipes are connected, partly as the pipe connection to the customer and partly as the customers own pipe system. The pipes used for pipe connection to the customer have often been kept outside, not uncommon with periods up to five years. Thereby corrosion products and pollutants can have occurred on the inner surface of the pipes. For net A, an increase of bacteria in the district water at

the third sampling occasion can be seen (diagram 2a). One explanation could be that the temperature of the district cooling water increases to temperatures more close to the optimum of the bacteria compared to the winter period of sampling number two. This explanation is however less likely since the concentration of the bacteria at the first sampling occasion also was low. A more plausible explanation to the increase of bacteria is instead a new connection at the end of 2002. This is also actually the case according to responsible personnel at the net.

For net B an interesting result could be seen when comparing the concentrations of viable bacteria in the biofilms and in the district water, diagram 2b. For the third sampling occasion the concentration in the biofilm increases heavily while at the same time the concentration in the district net decreases. Even if high concentrations in the district water not necessary means high concentrations in the biofilm- or vice versa- a decrease in the district water often implies a decrease in the biofilm, if the biofilm is in its initial state. This is due to the fact that the conditions for the micro-organism in the district water is more alike to the conditions for the micro-organism in the biofilm, if the biofilm is in its initial state. If the biofilm is fully developed a change in the environment, e.g. a decrease in the flow of nutrients, can influence the micro-organism in the district water more heavily compared to the micro-organism in the biofilm. A reason to the divergence for net B could therefore be that the biofilm here is fully developed, and has formed a stable and favourable environment for its micro-organisms. The biofilm could here develop in a very unfavourable way for the underlying material.

The variation in concentration during a period points out the risk with occasional samplings. If, for example, the sampling only had taken place in the beginning of March, the picture would have been much more positive- but only seemingly.

Finally it has to be said that it can be difficult with any higher degree of reliability to conclude what can be the reason for changes in the concentration of micro-organisms during an exposure period, if only a few samplings have been made. Partly this is due to the difficulty to exclude that the change is only apparent due to mistreatment of the samples. But even if the change pictures the real conditions of the net, it can be difficult to clarify the cause. Of especial interest is whether the change is temporary, e.g. due to temperature changes or more permanent, e.g. due to leakage of pollutants, pointing towards an even higher increase in concentration. For some of the results presented above, it would have been easier to draw the conclusions with additional sampling occasions. This is especially for net A (diagram 2a), net B (diagram 2b), net E (diagram 1e and 2e) and net F (diagram 2f). Following samplings could here have confirmed whether the change was temporary or not.

Corrosion and biofilm formation

No corrosion of considerable degree could be seen on the coupons in any of the exposure containers. The corrosion speed was estimated to only 1-2 μm per year, and no pitting corrosion could be observed. This is in accordance with the absence of SRB, which is the organism that is the most contributing to microbial corrosion in district cooling nets. SRB is a type of bacteria, which is anaerobic, and as such appearing mainly in oxygen free environments. However, oxygen free environments usually appear after a while in biofilms formed by aerobic bacteria. Relatively large concentrations of viable aerobic bacteria have been found in the district water and in the biofilms of the exposed coupons of the investigated district cooling nets. Therefore it is reason to believe, that

the absence of SRB probably is not due to conditions that means that SRB will not be formed. Instead there is probably only a matter of time.

MIC and biofilm detectors for on-line measurements

Microbial corrosion means corrosion occurring under influence from micro-organisms. Therefore, to estimate whether MIC is at hand or not, it is not enough to detect corrosion and a presence of micro-organisms. It also has to be verified that the presence of micro-organisms increases the corrosion rate. According to the title of this sub project, "Measurement and comparison of microbiological activity and corrosion rate", one idea to measure MIC is to simultaneously measure microbiological activity and corrosion rate. However, one argument against the possibility of this idea is that a change of the district water characteristic can simultaneously stimulate the corrosion rate and the microbial activity, thereby giving a misleading connection between the corrosion rate and the microbial activity. Another, and a more practical argument, is the difficulty of measure microbial activity with a detector, a thing which hardly can be made, especially not in such rather tough environments as a district net.

One characteristic of MIC is the difference between the water composition in the region at the metal surface under the biofilm and the water composition outside the biofilm. Therefore, another idea is to detect the concentration of corrosive components in the region between the metal surface and the biofilm. If corrosion is detected for a metal covered with a biofilm, and if a simultaneous verification can be made of a divergence between the concentration of corrosive components at the metal surface and the water composition outside the biofilm, the corrosion could be defined as MIC. This however, demands for probes capable of measuring the concentration of a large number of components, probes that also has to stand the environment of the district net.

A possible alternative could be to measure the corrosion rate at two metal surfaces of equal material. If only one of them is covered with biofilm and also has a higher corrosion rate, MIC could be stated. The problem then is to estimate whether a biofilm has occurred or not, and therefore there is a need for a biofilm detector too. A biofilm detector is however of interest, even if not used together with corrosion measuring devices. A biofilm is not only a requirement for MIC to occur, but can also, if formed at a heat exchanger, reduce the heat transfer efficiency of the heat exchanger. Unlike using the method with coupon exposure, a biofilm detector can at an early stage verify whether a biofilm has been formed or even if a risk of biofilm formation exists. Measures can then be taken which are both more efficient and less expensive.

The expectations of a biofilm probe are for the owner of the net to give a warning if biofilm has occurred or if the water quality is such that it stimulates formation of biofilm. For the scientist the expectations are somewhat more sophisticated in the sense that the biofilm probe should be able to grade the risk for biofilm occurrence for different water qualities. In both cases, the biofilm probe should be sensitive, accurate, quick in delivering descriptions of the environment, and resistant enough for the district net environment. For the owner of the net the probe should also be easy to install, to use and to interpret but also economical. For other techniques than those based on electrochemical measurements, such as heat transfer resistance and quartz crystal micro balance, the mentioned demands seem hard to fulfil.

For techniques based on electrochemical measurements, there is a need to distinguish between signals originating from changes in the water quality and signals originating from formation of a

biofilm. This could be done by the exposure of two probes but heavily reducing the risk for formation of biofilm on one of them. One way of eliminating the risk of biofilm formation is to use a dual-cell, where a probe is located in each cell but where one of the cells is illuminated by UV-light, thereby eliminating the micro-organisms. Another way is to expose one of the probes seldom enough to avoid biofilm formation, but still resulting in an efficient biofilm detector.

Also for techniques based on electrochemical measurements the mentioned demands of the probe excludes some techniques, e.g. noise measurements due to its rather low accuracy and its difficulty in interpretation. However, both the probe BioGeorge and the system BIOX are techniques based on electrochemical measurements, where both seem to be promising and are also available as commercial systems. One characteristic with BioGeorge, which can be seen as an advantage for the owner of the district net, is that BioGeorge stimulates the formation of biofilm if a potential for it exists, thereby giving a warning well before a biofilm has occurred in the district net. A more home made set up could also be possible to use, simply using two inert electrodes, where one is not exposed to the micro-organisms. Measuring the potential difference between the electrodes should give a signal when a biofilm forms on one of the electrode, since a biofilm would normally decrease the potential. It should also be possible to use a corroding electrode as the one exposed to micro-organisms. Here, on the other hand, an increase in potential should be expected if a biofilm is formed.

Summary

- ◆ Biofilms have been formed on all exposed coupons for all the six investigated district nets.
- ◆ Hazardous levels of the concentration of micro-organisms have been found for all the district nets, both regarding the district water and the biofilms formed on the exposed coupons
- ◆ To use district water that is degassed and unionised probably leads to a reduced risk for microbial related problems.
- ◆ The highest levels of micro-organisms has been found though, for the two nets which have a district water that have been degassed and unionised most rigorously. However, these two nets have added pyranine, a carbon compound, to the district water, and a likely explanation is therefore that pyranine acts as a nutrient source for the micro-organisms.
- ◆ No extensive corrosion was found on the exposed coupons, which is in accordance with the very low levels of SRB present in the biofilms. The condition for a large increase of the SRB concentration, and a following increase in corrosion, is unfortunately likely, due to the high concentrations of other micro-organisms found.
- ◆ It has clearly shown that there is a risk in drawing conclusions from the presence of micro-organisms after investigations made only occasionally or from analyses made only on the district water.
- ◆ An exposure container developed at the SCI has been used during phase 2 of the project. It has shown to be both functional and easy to handle for investigation of the potential for the district water to form biofilms, and to analyse the presence of micro-organisms in the biofilms formed.

Recommendations

- Only water of DH quality should be used, both as basic water and feed water.
- Avoid additives, especially if organic.

- Only connect pipes which are not contaminated on the inside.
- Watch over the system regarding micro-organism related problems, preferably by using exposure containers.

Future plans

In this subproject it has been concluded that it is likely that pyranine strongly contributes to the growth of micro-organisms. If pyranine is believed to be of importance to use, it could be worth doing to make sure the effects of pyranine, and then especially at the concentrations needed as the function of a leakage marker.

It has also been concluded that it is likely that new water distributing connection to the existing net often contributes to the growth of micro-organisms. This is especially the case if the pipes used for connection have been stored outside for a long time. Another possible cause to the entrance of pollutants is via a leakage from a customer. A continuous exposure with belonging analyses during a longer period could clarify the effects of new connections and leakage from customer.

In this part of the project only carbon steel has been exposed and without noticing any heavily corrosion problems. It has however been seen that the biofilms are of such a character that the conditions are fulfilled for creating a corrosive environment. An exposure during a longer period could clarify if, and in such a case to what extent, the carbon steel begins to corrode.

Other material than carbon steel is normally also used in district nets, for example copper and stainless steel, where especially stainless steel in some cases has shown to be more sensitive to microbial corrosion than carbon steel. To expose these materials in the same way as carbon steel mentioned above, could clarify the sensitivity for the respective material.

To study the biofilm formation by sample exposure means the same limitations as it does when estimating the corrosion rate by using weight loss measurements. To search for possible techniques to be used to detect the presence of biofilms in a district net faster than by using the sample exposure method, and thereafter investigating some of the more promising techniques in a district net, would therefore be of interest.

Subproject 6 Design of unit and monitoring in industrial systems

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Background

There is a need for a simple technique to measure and monitor corrosion rates and chemical water parameters in district heating and other closed water circulation systems.

It could be either instantaneous measurements or monitoring over a period of time. In both cases it is difficult, time consuming, expensive or sometimes even impossible to get admittance to the system. In practice this means that the resulting water chemistry in the system is not controlled and the corresponding corrosion rates of steel are rarely measured.

In these systems corrosion rates are usually measured by counting the number of corrosion damages of pipes, tanks and radiators. When penetration of the hardware occurs, it is too late and there is not enough information about the water composition in the previous period. The damage is the result of water treatment and other service condition parameters summarised perhaps over a period of 15 years. At the time of the damage you know that in the passed period you have also spoiled many other parts of the system. In the following damage investigation there is disagreement between the occurring damages and the actual water composition in the system and the service parameters, which the plant claimed to use.

Therefore, for technical and economical reasons, there is a need for a tool that allows a simple way of measuring. Part 6 of the current project has the purpose of designing a test-unit, which could be installed in industrial heating and cooling systems. It should be suitable to allow measuring and monitoring in the most appropriate way. The newest results of methods for corrosion monitoring and on-line chemical analysis are taken into account. Some methods are developed in other parts of this project.

Background for choice of test-unit design and discussion of desirable measurement technique

Normally the subject of internal corrosion in district heating and closed circulation water systems has limited scope, however if one collects all the corrosion phenomena that our institute has encountered over the past 35 years, one finds a large selection amassed.

Some of the corrosion types that may occur in the various materials making up closed circulation water systems can be seen in the enclosed table 4.6.1 below:

Table 4.6.1. Corrosion occurrence in district heating systems.

Steel	General corrosion (pipes) Crevice corrosion (bottom of radiators) Deposit corrosion (bottom of radiators and pipes) Environmentally induced cracking corrosion (pipes) Pitting corrosion (pipes) Microbial corrosion (pipes, radiators, other)
Copper	Sulphide induced corrosion (pipes) Corrosion fatigue (both internally and externally)
Brass	Stress corrosion (radiator valves and bleed off valves) Erosion corrosion (radiator valves) Dezincification (radiator valves)
Solders and Brazes	Sulphide induced corrosion (pipe joints) Bimetallic corrosion (pipe joints) Corrosion fatigue (pipe joints)
Stainless Steel	Pitting corrosion (heat exchangers) Stress corrosion (heat exchangers)

Crevice and deposit corrosion

These two phenomena can be encountered in different ways, but the most severe and most widespread damage is associated with inadequate water treatment and the subsequent corrosion attack on steel. The rate of general corrosion attacks on freely exposed steel surfaces will be very low in waters where the pH is increased to near 10, or if other corrosion inhibitors have been added to the water. Here the surface will be passive. But in crevices and under accumulated deposits the passivity cannot be maintained. Thus, the smallest supply of oxygen to the system water will result in corrosion of the surface under the deposit. Below the deposit an active corrosion area arises, an anodic region, in which iron dissolution occurs. On the nearest surfaces outside of the crevice cathodic areas will form where the oxygen is consumed. The large conductivity in the water means that a large part of the adjacent surfaces may become cathodic and hence the more extensive will become the corrosion attack. Thus the rate of corrosion in steel constructions is strongly dependent on:

- Oxygen concentration in the water
- Electrical conductivity of the water
- Passivation measures and pH
- Crevice geometry
- Deposit type (iron/iron, sludge and corrosion products, micro-organisms and biological films)
- Deposit quantity and extent

It is crevice and deposit corrosion of steel, which is hardest to avoid, these give most damage in circulating water systems and the highest costs in terms of expenses. Therefore, it is these corrosion types, toward which we will direct our monitoring systems, in this project.

Conversely, we know much about how other corrosion types can be minimized or even prevented by the application of good practices in ordinary systems.

In sulphide containing geothermic water matters are different. Here a small but unintended supply of oxygen will result in corrosion of copper and copper phosphorous brazing metals. Our measuring equipment is not primarily aimed at these systems, but can be modified for use in geothermic water.

Review of methods for the study of crevice and general corrosion in steel

It is the projects goal to find optimal and cheap methods to evaluate the lifetime limiting damage types that can be found in a system. Furthermore is it the goal to find suitable methods to determine the corrosion rate. An essential use will be the ability over short time to be able to evaluate what a change in the water parameters means for the corrosion rate of steel.

The ability to measure in a system that is working under an increased pressure (up to 10 bar) and high temperature (50 – 85°C) shall be created.

Therefore it is the purpose to construct a monitoring system that is suitable for collecting two types of data on-line:

- a. Analysis of chosen parameters of the water (most importantly: pH, oxygen concentration and conductivity)
- b. Determination of the steels corrosion rate on uncovered surfaces and under deposits (important: weight loss samples, crevice corrosion cell, ER-technique, bio film-probe, other electrochemical methods [e.g. LPR and EIS])

The test-unit must give the possibility of testing and developing various methods. Comparative investigations shall be used to optimise choice of method toward future monitoring. It will be optimal, if the unit that is developed during the project is both suitable for the development phase and for monitoring exercises on systems after the project's end.

On-line monitoring for water parameters shall always be compared with the plant's usual water analyses (total analysis) for water composition and the chosen use of water treatment methods (for example: use of tannins, alkalisation, softening, oxygen removal or others).

Other considerations to monitoring techniques

It will be purposeful to perform corrosion rate measurements on a side stream with a test-unit installed as by-pass.

It is the intention that the measurements give a picture of natural corrosion conditions within the system. Corrosion measurements should be performed at the same temperature and pressure as in the system and at the same water composition.

In practice, flow speed will influence the corrosion measurement results. The ability to choose to measure in bulk with a speed that simulates flow in pipes and to measure at very low water speeds and in stagnant water is useful, as particles can deposit and biofilms develop etcetera. Furthermore there shall be ability to measure on the surfaces that are covered by deposits and have contact with other parts of the steel surface that are uncovered and exposed in flowing water. The test-unit must have the ability to do this.

When corrosion rate is measured it is relevant to be able to measure instantaneous values and to be able to measure accumulated attack over a longer time period. For instantaneous values it is useful first to perform measurements after an “incubation period”, so the scales, precipitates, biofilms etc. have time to develop.

Measurements of water parameters require that temperatures and pressures are much lower. Furthermore, a constant small flow of the water is required, for the measurement. Therefore, the on-line measurement of water parameters must be made on a side stream of water, taken from the test-unit which and subsequently conditioned.

Measured results shall be capable of transmission via a data logger with modem to the corrosion laboratory. Hereby, checks can be made to ensure that all gauges function correctly. In addition temperature recording shall be undertaken.

It is furthermore a requirement of the test-unit that it is easy to install and simple to operate for the system owner.

The mentioned principle conditions have been incorporated into the chosen design of test-unit as described in the next chapter.

Design of prototype unit for corrosion monitoring

For practical and financially attractive corrosion monitoring in district heating systems it is essential to gain easy access to the system without having to close down a large part of it for insertion or withdrawal of probes or samples. Therefore an important part of monitoring corrosion in practice is to develop a unit, where different methods can easily be applied. The unit should meet several requirements. Primarily the environment inside the unit should have good resemblance to the actual conditions inside the heating system. Preferably it should also be possible to imitate “worst case” conditions in the district heating system.

Several designs have been discussed leading to the development of the prototype in figs. 4.6.1-2. The unit has been built as a bypass unit with a measuring chamber mounted with several pipe stubs for installing probes. Depending on design, probes can be installed directly into the flow or in sheltering tubes, which can be used for monitoring corrosion at low water velocity and beneath deposits. Pipes and measuring chamber are made from carbon steel. To ensure realistic flow conditions inside the measuring chamber the bypass unit has its own circulation pump with a flow

of 150-200 m³/day. This results in a water velocity inside the measuring chamber of app. 0.10-0.15 m/s. The probes applied in the top or at the side of the unit are placed directly into the water stream thus the actual velocity at the probe surface will be considerably higher than 0.10-0.15 m/s.

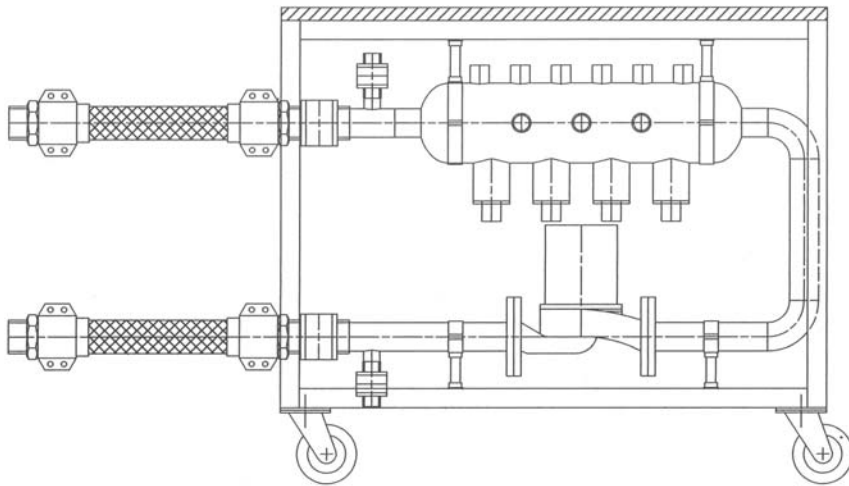


Fig. 4.6.1. Outline of unit prototype for corrosion monitoring in district heating systems.

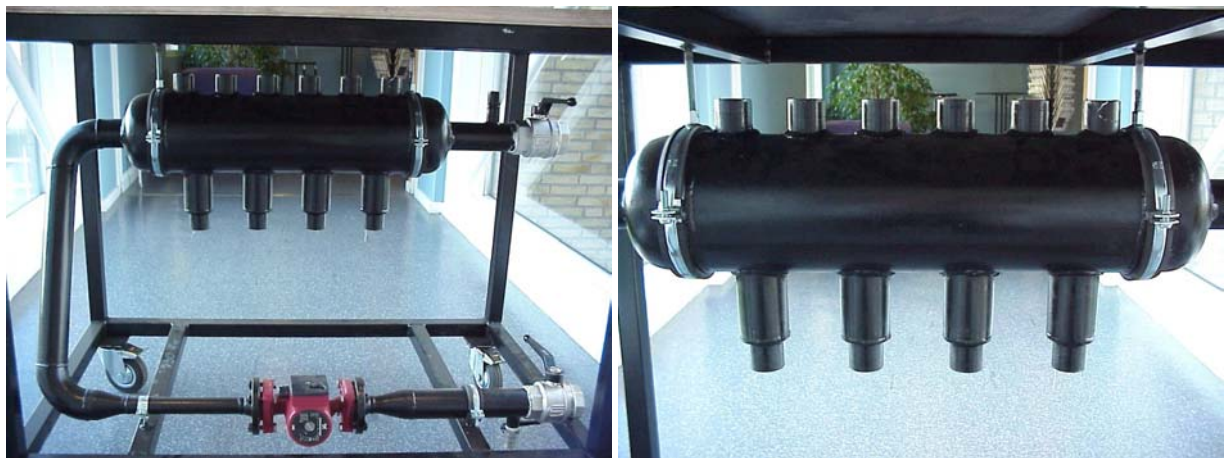


Fig. 4.6.2. Photos of the unit prototype. To the left detail showing the full bypass. To the right a close up showing the measuring chamber.

A separate portable panel with equipment for measuring conductivity, oxygen and pH has been developed. There are very high requirements to apparatus for accurate measurements in flowing water with very low conductivity and very low oxygen contents and for that reason a lot of effort has been put into choosing equipment. For measurements the portable unit is connected to the bypass unit and sample water is cooled in a sample-cooler to app. 25°C before measuring conductivity, oxygen and pH. Measurements are stored continuously in a data-logger and can be

monitored online parallel to the corrosion monitoring. The choice of using a separate panel for measuring conductivity, oxygen and pH has been made to ensure initial low expenses to the individual plant.

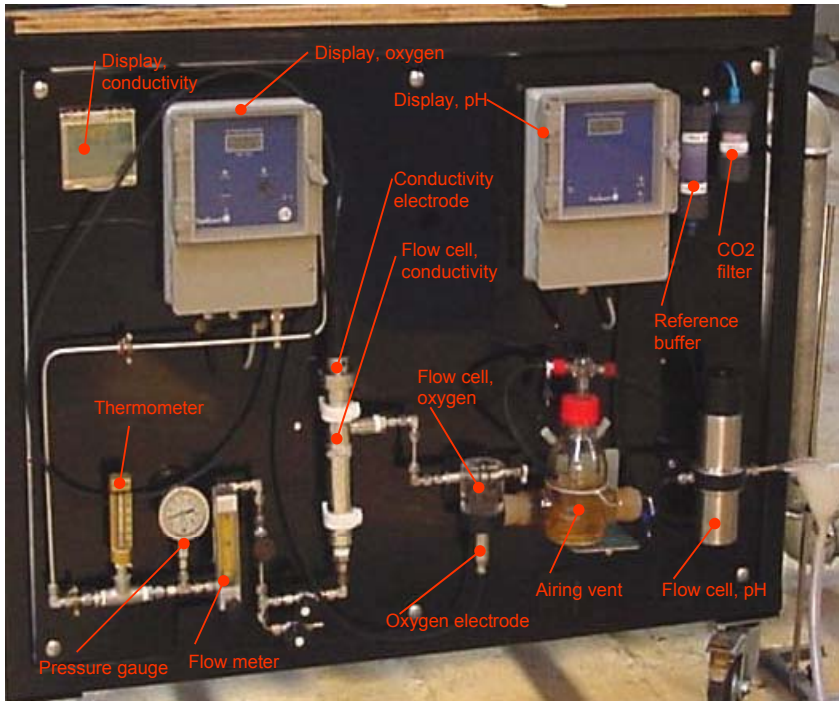


Fig. 4.6.3. Portable panel with equipment for measuring conductivity, oxygen and pH.

Selected technical specifications:

Conductivity

The system for measuring conductivity has been supplied by INSATECH A/S.

Model:	SC42-SP34, Yokogawa electrode SC150-A-S-AA. Yokogawa transmitter FF40-S22m, Yokogawa flowfitting
Temp. element:	Platinum resistor (Pt1000 to DIN)
Cell constant:	0.01 cm ⁻¹
Pressure rating:	10 bar/142 PSIG
Max. temperature:	150 °C
90% Temp. response:	< 1 min.
Measurement system	2-electrode system

Oxygen

The system for measuring oxygen has been supplied by OxyGuard International A/S.

Product name:	OxyGuard ppb
Type:	Self polarizing (galvanic) membrane covered amperometric cell
Sample temperature:	5°C to 50°C
Sample flow:	Depends on oxygen content and temperature - min. 50 ml/min, max 2000 ml/min
Sample pressure:	Atmospheric
Response Time:	20 sec for 0-5 and 0-80 ppb up-scale and down-scale. From 1 minute in air (calibration) to 100 ppb in approximately 40 sec, and to 10 ppb in less than 3 minutes.
Accuracy:	Error max. 0.5 ppb (or 3%).
Repeatability:	Better than 0.5 ppb (or 2%).
Conformity:	Linear.
Limit of Detection:	0.8 ppb.
Long term stability:	0.5 ppb (1 month)

pH

The system for measuring pH has been supplied by OxyGuard International A/S.

Product name:	OxyGuard Pure Water pH System
Sample temperature:	+5°C to 50°C recommended, 0 to 80°C acceptable
Sample flow rate:	Approx. 100 ml/minute.
Sample pressure:	The measurement should ideally be kept pressureless
Volume of sample cup:	200 ccm
Electrolyte reservoir:	Included, contains 135 ml
Electrodes:	Two paired glass electrodes
Range:	pH 4.00 to 14.00
Accuracy:	0.5% or 0.05 pH
Repeatability:	0.25%

Pre-experiment at DTU and FORCE Technology

The first prototype of bypass unit was placed at DTU. The panel equipped with chemical analysis instruments was first placed on the test unit at DTU. All the experiments are described in this report, Sub project 3.

The test panel for chemical analysis was removed from DTU and installed at the district heating system at FORCE Technology. The instrumentation was tested before the actual use at Ballerup.

Establishing of prototype unit in heating system in Ballerup

The bypass unit was established on 19 July 2002 at Ballerup. The unit was connected to the main return stream in the heating system.

Water treatment in the Ballerup heating system consists of pH adjusting and a tannin additive. The return stream temperature during the period of measuring was between 50°C and 51°C.

Make up water consumption	Make up water	District heating water Conductivity etc.
Small	Make up water is applied directly from Vestforbrændings supply system. Water is treated with tannins in alkaline solution (tanninphos).	Measured: Low in oxygen 385 $\mu\text{S}/\text{cm}$, 20°C pH 10.1

The bypass unit was equipped with weight loss probes (5 pieces), ER-probes (2 pieces), crevice corrosion cell (1 piece) and Three-electrode probes (2 pieces). One of the weight loss probes is meant for bio analysis. Probes were installed as shown in Fig. 4.6.4.

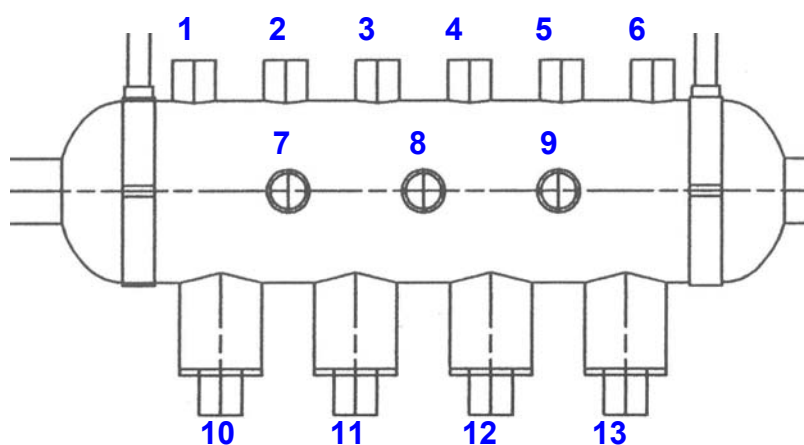


Fig. 4.6.4. Positions of probes in prototype unit in Ballerup. 1: Three-electrode. 2: Weight loss coupon. 3: Weight loss coupon. 4: Weight loss coupon. 5: Weight loss coupon. 6: Weight loss coupon. 7: Empty. 8: Empty. 9: Empty. 10: Crevice corrosion cell. 11: ER-probe. 12: Three-electrode. 13: ER-probe.

The panel for measuring conductivity, oxygen and pH as well as all the instrumentation for ER-technique and electrochemical measurements were installed on the bypass unit on 22 August 2002 by FORCE Technology, DTU and MetriCorr.

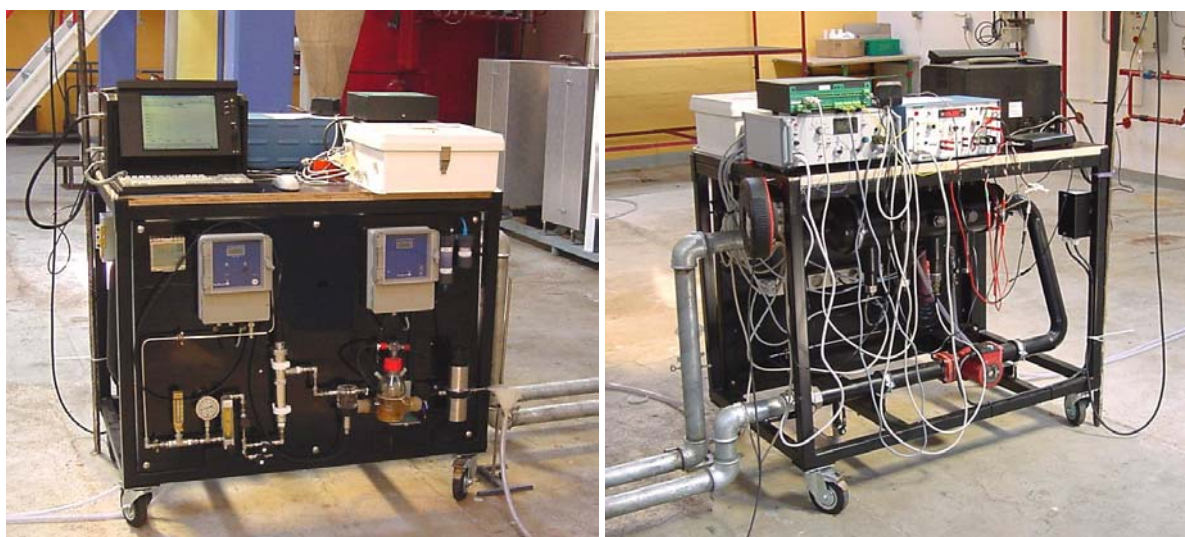


Fig. 4.6.5 The bypass unit fully equipped. The portable panel is attached to the bypass unit for measuring conductivity, oxygen and pH online. Equipment on top of the unit is instrumentation for ER-technique and electrochemical measurements. Results from corrosion measurements are stored in a data-logger and can be monitored online along with the water's conductivity, pH and oxygen content.

Measurements in Ballerup

Measurements were started 22 August 2002 and after a three week running-in period all necessary adjustments were made to the equipment. Results from measurements of conductivity, oxygen, pH and weight losses are shown on the next page. Results from the crevice corrosion cell, ER-probes, bio analysis and electrochemical measurement are discussed elsewhere.

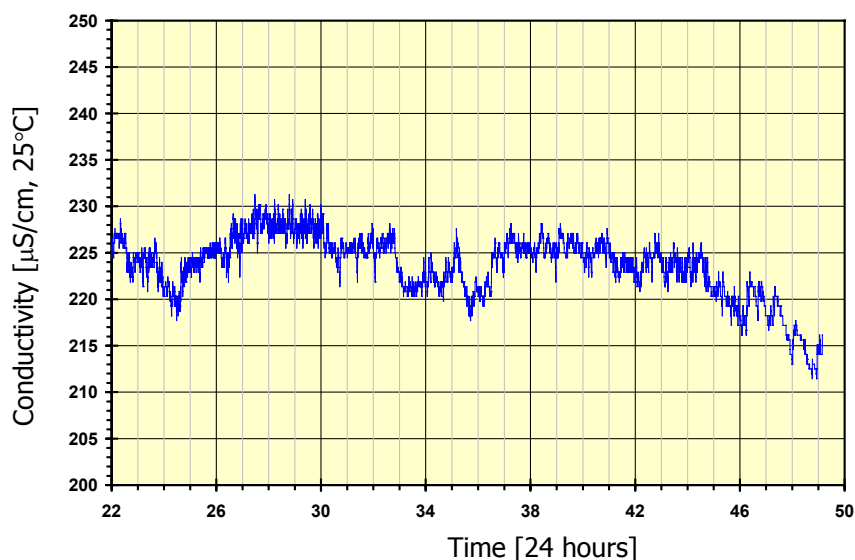


Fig. 4.6.6. Conductivity measured in the return stream in Ballerup heating system. The conductivity shows only small fluctuations. Sample flow: 100 ml/min. Sample temperature 22°C. Measurements have been stored every five seconds.

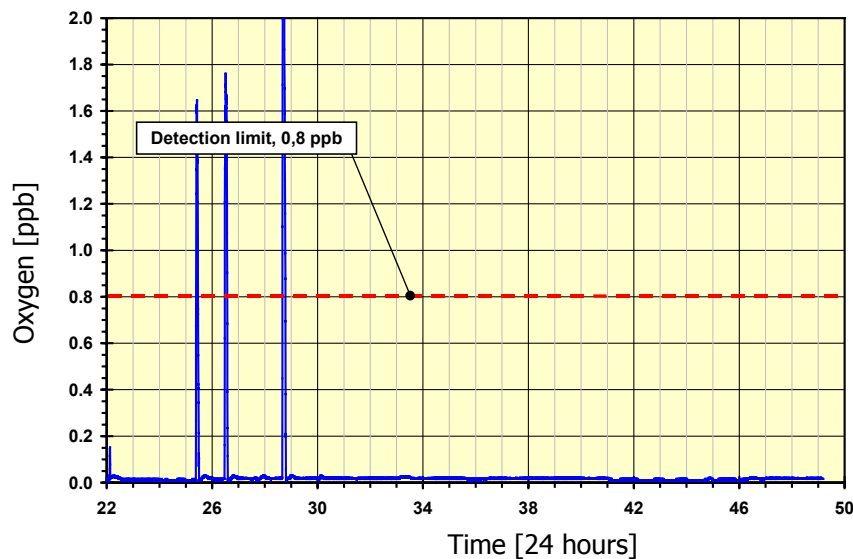


Fig. 4.6.7. Oxygen measured in the return stream in Ballerup heating system. The measured content of oxygen was generally lower than the equipment's detection limit (0.8 ppb). On three occasions the content exceeded 0.8 ppb but only for a few hours. Sample flow: 100 ml/min. Sample temperature 22°C. Measurements have been stored every five seconds.

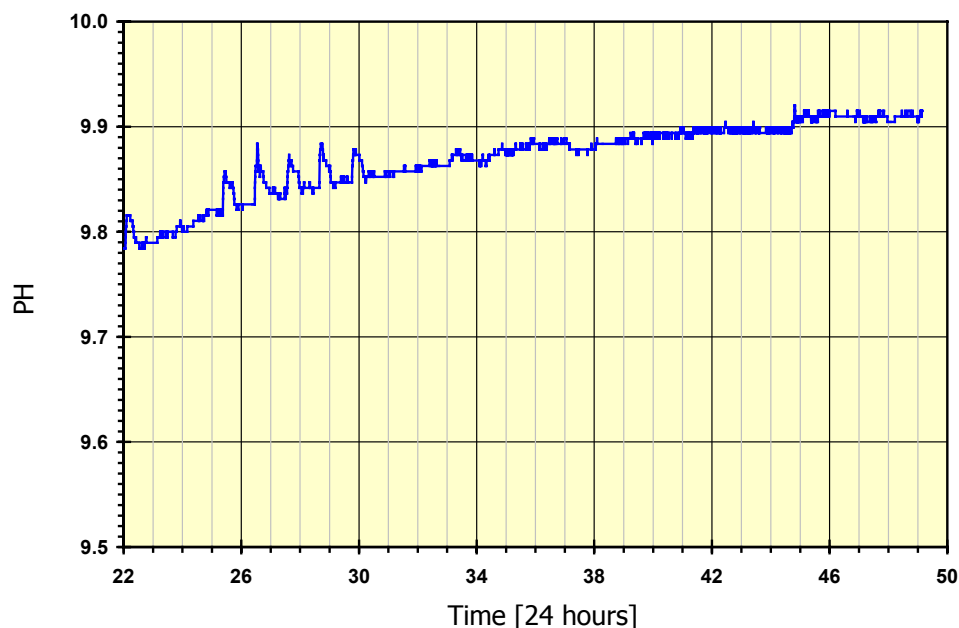


Fig. 4.6.8. pH measured in the return stream in Ballerup heating system. The measured pH value was very stable although showing a faint rise over the measuring period. Sample flow: 100 ml/min. Sample temperature 22°C. Measurements have been stored every five seconds.

Two weight loss coupons exposed in Ballerup have been evaluated with regard to corrosion. The coupons showed weight losses of 15 to 19 mg after 103 days exposure corresponding to an average corrosion rate of 2.7 to 3.4 $\mu\text{m}/\text{year}$. Corrosion attacks were only visible at the edge of Teflon washers and under the thermoplastic holder. There was no visible corrosion on the free surfaces.

Redesign of unit for corrosion monitoring

Experiences gained from measurements in Ballerup have led to changes in the unit design as well as small changes of the weight loss probes. Primarily the number of pipe stubs has been increased. But changes have also been made to make emptying and filling of the bypass unit more convenient.

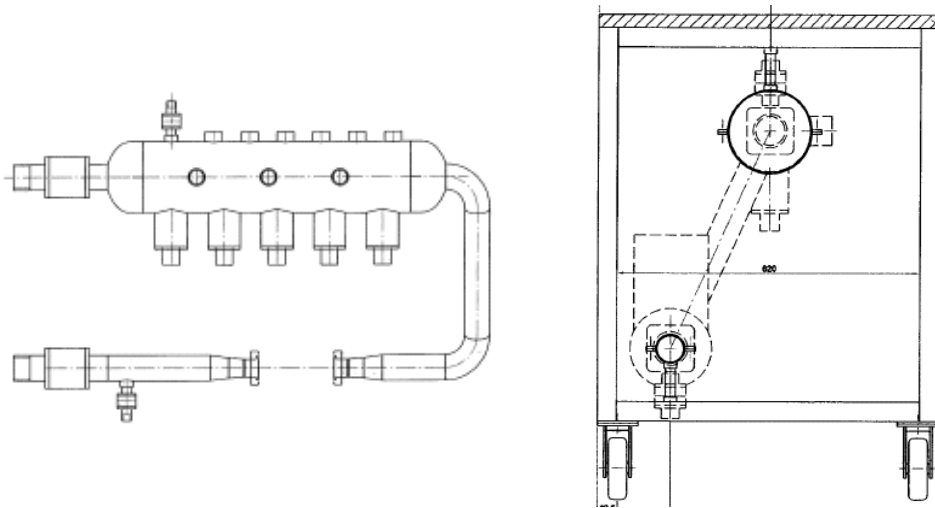


Fig. 4.6.9. Outline of redesigned unit for corrosion monitoring in district heating systems.



Fig. 4.6.10. Redesigned bypass unit shown without probes.



Fig. 4.6.11. New design of weight loss coupons with carbon steel disc for bio analysis.

Subproject 6A, Corrosion monitoring in industrial systems

Six bypass units with new design have been manufactured and the units have been installed at six different plants. The bypass units are equipped with weight loss probes (5 pieces with carbon steel disc for bio analysis), ER-probes (2 pieces + 1 with simulated deposits/crevice), crevice corrosion cell (1 piece) and three-electrode probes (2 pieces). Probes were installed as shown in Fig. 4.6.12.

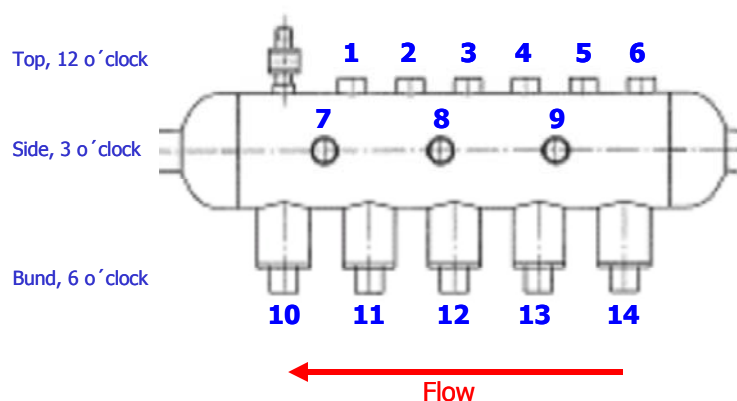


Fig. 4.6.12. Probe locations in bypass-unit.

- 1: Weight loss coupon including steel disc for biofilm analysis
- 2: Empty
- 3: Three- electrode.
- 4: ER-probe
- 5: Weight loss coupon including steel disc for biofilm analysis
- 6: Weight loss coupon including steel disc for biofilm analysis
- 7: LOCOR-CELL
- 8: Thermo sensor
- 9: Empty
- 10: Weight loss coupon including steel disc for biofilm analysis
- 11: ER-probe with simulated deposits/crevice
- 12: Weight loss coupon including steel disc for biofilm analysis mounted in an extended bottom branch piece for simulation of a dead end
- 13: Three electrode
- 14: ER-probe.

Participating industrial plants

The participating plants represent a number of different water treatments. An overview is seen in the enclosed table. A more detailed description is found in measuring reports in appendices.

Plant	System	Make up water consumption	Make up water		District heating water Conductivity etc.
Næsbyhoved-Broby varmecentral Odense Kommunale Fjernvarmeforsyning	Distribution system App. 2x2200 km main piping.	700 – 800 m ³ /24h	97% RO-water from Fynsværket. 3% cat-ion exchanged or in other way treated make up water from district heating plants.	Vacuum venting. Experiments with micro-bobble venting are carried out in small scale (1.5 ppm O ₂).	Low in oxygen 40 – 80 µS/cm
VEKS Vestegnens Kraftvarmeselskab I/S	Small distribution system.	Supplies make up water to distribution systems. According to statistics app. 50 m ³ /24h	Supplied from VEKS transmission system.	Requirements: <20 pbb O ₂ <20 µS/cm pH 9.7 ± 0,2	Measured 0 pbb O ₂ 80-90 µS/cm pH 9.2-9.4
Aalborg Aalborg Fjernvarmeforsyning	Distribution system App. 1200 km main piping.	App. 550 m ³ /24h	Earlier total desalinated water was supplied from Nordkraft (Aalborg midtown). Now total desalinated water is supplied from Nordjyllandsværket. September 2001 a new RO-plant has been bought into use.	Vacuum venting. Requirements: <100 pbb O ₂ <10 µS/cm	Requirements: 0 pbb O ₂ <50 µS/cm Measured: -10 pbb O ₂ 35-45 µS/cm
Viborg Energi Viborg A/S & Viborg Kraftvarme A/S	Transmission system. App. 12 km main piping.	Supplies make up water to distribution systems. Total consumption year 2000 was 2000 m ³ corresponding to 5,5 m ³ /24h	Make up water is produced through cat-ion exchanging followed by reverse osmosis.	Thermal venting. Measured: 75 pbb O ₂ 3.5 µS/cm	Measured: 0 pbb O ₂ (100 pbb) 30 µS/cm pH 9.5-9.7
H. Lundbeck A/S	Cooling plant. Closed system.	App. 350 l/month	RO-plant Originally filled with drinking water (aerated and filtered groundwater).	No venting of make up water.	Measured 2000: 382 µS/cm ved 25°C < 20 pbb O ₂
H. Lundbeck A/S	Central heating system.	Unknown	Drinking water (aerated and filtered groundwater).	Make up water is applied directly from the drinking water distribution system.	

Monitoring of corrosion, pH, conductivity and oxygen at seven plants

Units have been mounted in seven different plants and corrosion monitoring and measurements of pH, conductivity and oxygen have been carried out according to the table below.

Plant		Mounting of bypass unit	Intensified measuring period	End of measurements
Odense Distribution	Næsbyhoved-Broby Varmecentral	13. December 2002	13. January - 17. February 2003	26. February 2004
VEKS Distribution	Karlsunde Varmecentral	13. February 2003	28. February - 27. Marts 2003	18. February 2004
Aalborg Distribution	Svendborgvej varmecentral	9. Marts 2003	9. April - 30. April 2003	1. Marts 2004
Viborg Transmission	Viborg Kraftvarmeværk	19. June 2003	6. August - 1. September 2003	1. Marts 2004
H. Lundbeck A/S	Cooling plant. Closed system.	14. October 2003	21. October - 11. November 2003	5. Marts 2004
H. Lundbeck A/S	Central heating system.	14. October 2003	11. November - 9. December 2003	5. Marts 2004

All probes in the bypass unit have been exposed to the circulating bulk water during the period from mounting the bypass unit to the end of measurements. Online measurements have been made only in the intensified measuring period. The end of measurements indicates the ended exposure of the weight loss coupons.

After ended measurements a report presenting results and conclusions from each plant was sent to the plant owners and plant owners as well as technical personnel have attended a seminar where all results and experiences have been discussed.

Results

See appendices regarding the results obtained from measurements made at seven different pants in the bypass unit.

After termination of the measurements the LOCOR electrodes were examined microscopically to evaluate the corrosion attacks. The active anode area only constituted 10-15% of the total area, and consequently the calculated corrosion rates shown in the appendices are too high. The true corrosion rates are 6-10 times as high at the tabulated values. It is now found that the corrosion rates are much higher than the ER corrosion rates. This is in good agreement with the different forms of corrosion measured by the two measurement methods.

Conclusions

The overall result for all works is that highly sensitive ER (electric resistance) measurements are suitable for surveillance of general corrosion velocity and the LOCOR cell (crevice corrosion current) is suitable for surveillance of local corrosion risks. Both techniques have reacted fast to environmental changes in the systems and make possible continuous corrosion monitoring.

Highly sensitive ER may be interpreted as electronic weight loss measurements that on-line trace continuous variations in corrosion velocity over very short periods

(hours). In comparison, credible weight loss measurements in such systems have required a measuring period of minimum 6 months.

Changes in crevice corrosion current measured with the LOCOR cell have clearly indicated the presence of localised corrosion. Conversion of the measured corrosion current to corrosion rate is difficult, as it requires knowledge of the area of the active anode. The LOCOR cell gives response to changes in the risk of local corrosion within minutes and the results can thus be compared directly to changes in operation.

Two electrochemical methods – linear polarisation resistance (LPR) and electrochemical impedance spectroscopy (EIS) – have been applied primarily for mechanism studies. The LPR method is used for commercial continuous corrosion surveillance/detection, but it is not recommendable in district heating systems, as it has resulted in a strong tendency to overrate the corrosion velocity. In general, the EIS method has resulted in more credible corrosion velocities but analysing the data is demanding and the measuring period is too long (several days) to register sudden changes.

The separate portable panel with equipment for measuring conductivity, oxygen and pH gave good results and the equipment proved suitable to use in district heating systems and other closed circulating systems. Less advanced equipment to measure pH will be adequate in many cases. To obtain reliable data, experience showed that it is of utmost importance that flow and temperature of the sample water are stable. The equipment to measure oxygen was surprisingly reliable and needed less maintenance than expected, thus monitoring oxygen in the bulk water should be considered as a supplement to the more common measurements of pH and conductivity. Equipment to measure oxygen should preferably be mobile, making it possible to conduct periodic measurements where problems are suspected or to locate oxygen ingress.

Measurements of corrosion rates and water quality showed that the corrosion rate was negligible in waters with low or no oxygen. High pH and low conductivity reduced the risk of corrosion damages in systems where periodic oxygen ingress was observed due to makeup water addition.

Future work

The results obtained during corrosion monitoring in Danish district heating plants have showed that corrosion monitoring can be applied successfully and that corrosion monitoring complements the traditional monitoring of pH and conductivity.

In the future weight loss coupons, ER-probes and the LOCOR cell can be applied in district heating plants as part of the normal operation. Further work on the LOCOR cell design and results obtained from longer periods of exposure in different water qualities will improve the interpretation of data.

For the benefit of the Danish district heating industry the obvious future project would be cooperation between Danish Technological Institute, MetriCorr, DTU and FORCE Technology combining monitoring of microbially induced corrosion with continuous corrosion monitoring in the form of high sensitive ER and the LOCOR cell.

V Conclusion

The project has run satisfactorily and in agreement with the original plan. The synergistic effect in the project has been significant. The subprojects have dealt with different aspects of the corrosion and scaling problems and the participants thereby have got more information and better understanding.

The group has been successful in presenting the results. The participants have been active in contacting each other and some have visited laboratories in other countries studying applied methods. Eight engineering students have been active in the project. Moreover, contacts have been made with researchers with similar interests outside the project group. A demonstration experiment was organized in Denmark and Iceland for testing a commercial electrochemical monitoring set-up SmartCET[®] from Intecorr, a US company. The methods used were LPR, HDA and EN in one box and including automated analysis. The results were compared with other obtained results and the applicability of the equipment was evaluated for district heating systems, both for uniform corrosion measurements and for localized corrosion estimation.

The project has resulted in development of suitable methods for online monitoring of corrosion in district heating and cooling systems. It is recommended to use two methods simultaneously for monitoring, ZRA and either LPR or high sensitive ER. ZRA detects rapidly changes in the water chemistry of importance for corrosion, e.g. ingress of oxygen and can alarm if the level goes beyond a prescribed level. Furthermore, ZRA can estimate the danger of local corrosion attacks. LPR and high sensitive ER informs about the corrosion rate. In case of LPR it is of importance to know the optimal parameters and algorithm for calculating the polarisation resistance.

The SmartCET[®] from Intecorr did not provide reliable results on the corrosion rate in the systems, but the EN measurements could give information about local corrosion and sudden changes in the system. Thus, EN could replace ZRA for detecting changes in the water chemistry and estimate the local corrosion in the system.

The application of the EIS technique can not be recommended since consistent results were not obtained. The evaluation of the results is complicated and prone to miscalculations.

Online oxygen monitoring was successful in all places except for the geothermal sulphide containing distribution systems in Iceland, where the sulphide interferes. It is therefore recommended as a supplement to measurements of water parameters. In the geothermal systems however the equipment to measure oxygen was not reliable and needed a lot more maintenance than expected. Ampoules for oxygen measurements need to be used in those systems until a more reliable online monitoring system has been developed. ZRA or EN together with online conductivity measurements can prove especially successful for quality control in these systems.

Combining the CV and/or optical measurements by camera to other techniques may be useful in studying the reactions of e.g. sulphur compounds in district heating water and for monitoring film formation.

Detection of microbial corrosion by online methods is hardly possible and the use of coupons is preferred. Biofilm is formed on all exposed coupons and it will always be difficult to relate corrosion problems directly to micro-organisms. However, the developed online methods will measure the corrosion rate and follow changes in the system, regardless of the corrosion causes.

Evaluation of results

The five goals that the Nordic Industrial Fund has established for the projects it funds or supports are:

- Pioneering the exploitation of the synergistic networks through innovative systems
- Cutting-edge innovation in efficient infrastructure for small and medium-sized enterprises
- Models for management issues and business culture
- Strength in international pre-normative work
- Pioneering in areas which have been identified as being of importance for the Nordic skills market

The results in these areas are expected to demonstrate results or influence in at least one of these five areas. The results are to be graded on a scale of 1-5, where 1 represents no correspondence and 5 represents total correspondence.

A) Pioneering in the exploitation of synergistic networks through innovative systems

	Evaluation scale 1-5
The project has generated an efficient and beneficial structure between the players in the Nordic cooperation.	4

The project has established and increased communication between Nordic researchers in the areas of corrosion monitoring, microbial corrosion, instrument design and district heating systems. The increased communication between the Nordic researchers that are specialized in different areas lead to synergy effect and thereby better work, which should be of value to the district heating industry. Furthermore, the collaboration between project partners strengthens in general and will doubtless increase the future correspondence between laboratories.

The Scandinavian corrosion congress was held in Reykjavik in April 2004. The congress is a revival of a tradition back to 1954, but has not been held since 1992. Also a course for Ph.D.-students was held in Reykjavik in April about online corrosion monitoring in industrial systems. There were 22 participating students and 5 lecturers.

B) Cutting edge innovation in efficient infrastructure for small and medium-sized enterprises

	Evaluation scale 1-5
The project has contributed to an improvement of the business climate and the opportunities for internalisation for small and medium-sized enterprises.	3

The project is expected to be of considerable help to industrial partners that are designing instruments for corrosion measurements and/or instruments to measure

water components. Furthermore, increased knowledge in the field is of value to advisers, researchers and district heating companies.

C) Models for management issues and business culture

	Evaluation scale 1-5
The project has contributed to developing the management style within the Nordic countries, to the dissemination of a democratic business culture, and to the competitive advantage and goodwill for the Nordic countries from a global perspective.	3

The project work has strengthened the already good Nordic skills in the district heating industry. The press releases lead to inquiries about the project from the Baltic countries and Germany and presentations at ICC in Granada in September 2002 about the project got interest from researchers from USA and some other countries. A unit SmartCET[®] from Intercorr in USA was tested in Denmark and Iceland.

D) Strength in international pre-normative work

	Evaluation scale 1-5
The Nordic development work within the project has created basis for forthcoming international norms.	2

The interest from district heating companies in the project is in line with the companies' increased emphasis on quality control. The work of the project is likely to be of interest for forthcoming international norms.

E) Pioneering in areas which have been identified as being of importance for the Nordic skills market

	Evaluation scale 1-5
The project has contributed to a world-class skills market within the area considered important for Nordic business life and the public sector.	4

The project has established collaboration between researchers and industry partners with different background. Exchange of ideas, fruitful discussions and research work increases the knowledge of the project participants and increases the cooperation between the countries. Doubtless the cooperation between laboratories will increase in the future, even in other related areas.

The Nordic countries are already known for their skills in district heating and cooling and online real-time corrosion monitoring methods may further increase the industries' competitiveness.

Dissemination of information and results

A) The project has implemented the information activities, which were laid out in the approved plan. Press releases were sent out at the projects start and articles have been published and furthermore the results of the project were presented at The International Corrosion Congress in Granada Spain 22.-27. September 2002, Eurocorr 2003 in Budapest Hungary 28. September – 2. October 2003 and the 13. Scandinavian Corrosion Congress in Reykjavik Iceland 17.-20. April 2004. Moreover the results have been presented at a course for Ph.D.-students in Reykjavik 15.-18. April Corrosion monitoring in industrial systems. The course was supported by NORFA. The activities are listed under C)

B)

Target groups	Opinion (For example: media, interest groups)	R&D (For example: strategic and grant awarding bodies, R&D institutes, universities)	Politics (For example: Nordic or national politicians, political or administrative leaders)	Business (For example: Customers, allies, competitors, R&D managers, line managers and consultants)
Activities: (Web sites, newsletters, press releases, letters, conferences, workshops, publications, presentations, TV, radio, newspapers, etc.)	Web site Press releases Newsletters	Web site Press releases Publications Newsletters Presentations Direct contact International Corrosion Congress	Web site Press releases Newsletters Direct contact	Web site Press releases Publications Direct contact Presentations
Results of activities: (published articles, inquiries, political reactions, commissioned reports, expressions of interest from other R&D bodies, etc.)	Published articles	Inquiries from the Baltic countries, Germany and USA		
Actual costs against information budget (actual versus budgeted costs)	NOK 80.000 (actual) / 7.000 (budgeted).			
Self-evaluation of activities (1-5)	3	4	4	3

C) List of published articles and presentations during the project.

Articles:

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2. Thorarinsdottir, R.I., *Corrosion measurement and improved quality control in district heating systems*. ScanVac Newsletter 1/2001.
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5. Nielsen, K., *Monitoring of corrosion in district heating systems (In Danish: Monitering af korrosion i fjernvarmesystemer – Nyt nordisk samarbejdsprojekt støttet af Nordisk Industrifond)*. Nordisk Korrosion nr. 2/2001.
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8. Forsén, O., *Corrosion measurements in district heating systems, project part 3*. Nordicinnovation News Letter, March 2002.
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10. Andersen, A., *Monitering af korrosion i fjernvarmesystemer (KORMOF)*. Submitted to Nordicinnovation Newsletter in November 2002.
11. Korsbæk, K., Rubæk, R. Andersen, A., *Monitering af korrosion i fjernvarmesystemer*. Nordisk Korrosion Nr 3/2002.
12. Thorarinsdottir, R.I. and Hilbert, L.R., *Corrosion monitoring in district heating systems – results from a Nordic research project*. Submitted to Danish Board of District Heating (DBDH) in May 2004.

Reports:

1. Project reporting to Nordicinnovation, *Monitoring of corrosion in district heating systems*. Project no. 00071, Report no. 1, January 2002.
2. Højman, A. and Lind, P.S., *Korrosion i fjernvarmesystemer*. IPL, The Technical University of Denmark, January 2002.
3. Houlberg, M., *Korrosion i fjernvarmeanlæg*. IPL, The Technical University of Denmark, June 2002.
4. Rubæk, R. og Korsbæk, K., *Praktikrapport om korrosionsmonitoring i fjernvarmesystemer*. FORCE Technology & DTU, Denmark, 2003.
5. Norskov, L., *Comparative studies of the reliability of electrochemical techniques in geothermal water*, IBRI, Iceland, January 2003.
6. Project reporting to Nordicinnovation, *Monitoring of corrosion in district heating systems*. Project no. 00071, Report no. 2, May 2003.

Seminars/congresses:

1. Richter, S. and Thorarinsdottir, R. I., *Corrosion monitoring in district heating systems*. The 8th International Symposium on District Heating and Cooling in Trondheim, Norway, August 2002.
2. Hilbert, L.R., Thorarinsdottir, R. I., Andersen, A. and Nielsen, L.V., *Optimising corrosion monitoring in district heating systems*. ICC 2002 in Granada, Spain September 2002.
3. Thorarinsdottir, R.I., *Corrosion of copper alloys in geothermal district heating systems*. ICC 2002 in Granada, Spain, September 2002.
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5. Richter, S. and Hemmingsen, T., *A study of the electrochemical behaviour of sulphur compounds*. Eurocorr 2003 in Budapest, Hungary, September 2003.
6. Hemmingsen, T., Hilbert, L. and Nielsen, L.V., *Assessment of sulphur and H₂S corrosion by the use of simultaneous ER, galvanic and optical measurements*. Eurocorr 2003 in Budapest, Hungary, September 2003.
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10. Hemmingsen, T., *A comparison of sulphur reactions in saline and nonsaline electrolytes on carbon steel*. Poster presented at 54th Annual Meeting of the International Society of Electrochemistry in Sao Pedro, Brazil, August 2003.
11. T. Hemmingsen, Austvoll, I. Fusek, F. and Skavås E., *Combined optical and electrochemical measurements on sulphide film formation*. 13th Scandinavian Corrosion Congress, Reykjavik, Iceland, 17.-20. April 2004.
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13. Andersen, A., Nielsen, K., Hilbert, L.R. and Nielsen, L.V., *Development of a unit suitable for corrosion monitoring in district heating systems*. 13th Scandinavian Corrosion Congress, Reykjavik, Iceland, 17.-20. April 2004.
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16. Richter, S. and Thorarinsdottir, R.I., *Comparing LPR and EIS in low-conductivity water systems*. 13th Scandinavian Corrosion Congress, Reykjavik, Iceland, 17.-20. April 2004.
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Seminars:

1. Nielsen, K. and Andersen, A., Seminar for industrial partners in Denmark, FORCE Technology, September 5th, 2001.
2. Thorarinsdottir, R.I., *Electrochemical corrosion measurements in pipe systems. (In Icelandic: Rafefnafræðilegar tæringarmælingar í lagnakerfum)*, Seminar: Samorka (Federation of Icelandic Energy & Waterworks) Orkuþing, Akureyri, Iceland, October 11-13, 2001.
3. Nordling, M., "Kyldagen" ("The Cooling Day") 26/4 2002, organised by "Svenska Kyltekniska Föreningen", ("The Swedish Refrigeration Technology Association").
4. Nordling, M., "Temadagar Fjärrkyla" ("Thematic Day of District Cooling") 30/5 2002, organised by "Svenska Fjärrvärmeföreningen" ("The Swedish District Heating Association").
5. Richter, S., *Electrochemical corrosion measurements*. Icelandic Centre for Building Installations, June, 2002.
6. Hemmingsen, T., *Monitoring av korrosjon i fjernvarmeanlegg- Et Nordisk Samarbeidsprosjekt*. Norsk Korrosjonsteknisk Forening, November 6, 2002
7. Hemmingsen, T., *Monitoring av korrosjon i fjernvarmeanlegg- Et Nordisk Samarbeidsprosjekt*. Norsk Korrosjonsteknisk Forening, November 6, 2002
8. Hemmingsen, T., *Fjernvarme - utfordringer og muligheter*. Norsk Kjemisk Selskap, Februar 5, 2003
9. Hemmingsen, T., *Elektrokjemiske studier omkring svovel*. Dansk Korrosionsteknisk Selskab, April 3, 2003
10. Richter, S., *Monitoring corrosion in district heating systems*, The University of Iceland, November 2003.
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12. Hemmingsen, T., Hilbert, L.R., Thierry, D. Kane, R.D. and Thorarinsdottir, L.R. *Course for Ph.D.-students – Corrosion monitoring in industrial systems*. Reykjavik, Iceland, April 2004.

Web-sites:

1. <http://prosjektweb.nordicinnovation.net/news/default.asp?proID=96>
2. <http://www.rabygg.is/d/lagna/rannsoknaverker.asp>
3. http://www1.his.no/vit/tn/hemmingsen/Projectproposals_2001.htm
4. <http://imn.ux.his.no>

Administrative and statistical data

Number of participants from:	Public authorities, research funding organisations		Business Companies and organisations		Universities and research institutes	
	Number of participating organisations	Number of participants (individuals)	Number of participants companies and organisations	Number of participants (individuals)	Number of participating universities and institutes	Number of participants (individuals)
Denmark			10	14	2	6
Finland			2	2	1	2
Iceland			3	3	2	2
Norway			1	1	1	5
Sweden			3	3	2	2
Baltic countries, Russia						
Non-Nordic EU countries						
Other countries				1		1
Total participation			19	24	8	18
Number of participating companies with fewer than 50 employees						4
Number of participating companies with more than 50 employees						23
Did the project run to schedule? (please mark the correct answer)						
						Yes No
If no, how big were the deviations (in months)?						
Cooperation activities and meetings						10 (2 with all countries)
Number of seminars, workshops, courses during the year						4
Number of participants at seminars, workshops, courses run during the year						100

If relevant to the project, please answer the following:

Number of patents and patent applications submitted during the year	
Number of product and process enhancements introduced to the industry	
During the year	
Since the start	
Number of prototypes developed during the year	1

Reporting of deviations from the standard conditions

In the second year there was some delay in in-situ testing (2 months), as there was need for more pre-work. In the last year the project work has followed the plan and the final report is only 1.5 month delayed.

Financial statement

Statement of account (regnskabsrapport) is sent separately.

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Appendices

Measuring reports from Aalborg distribution system, Lundbeck cooling system, Lundbeck central heating system, Odense distribution system, VEKS distribution system and Viborg distribution system.

Measuring report from Aalborg distribution system

Monitoring of corrosion in district heating systems (KORMOF)

Joint Nordic Project with support from Nordisk Industrifond (Nordic Innovation Centre)

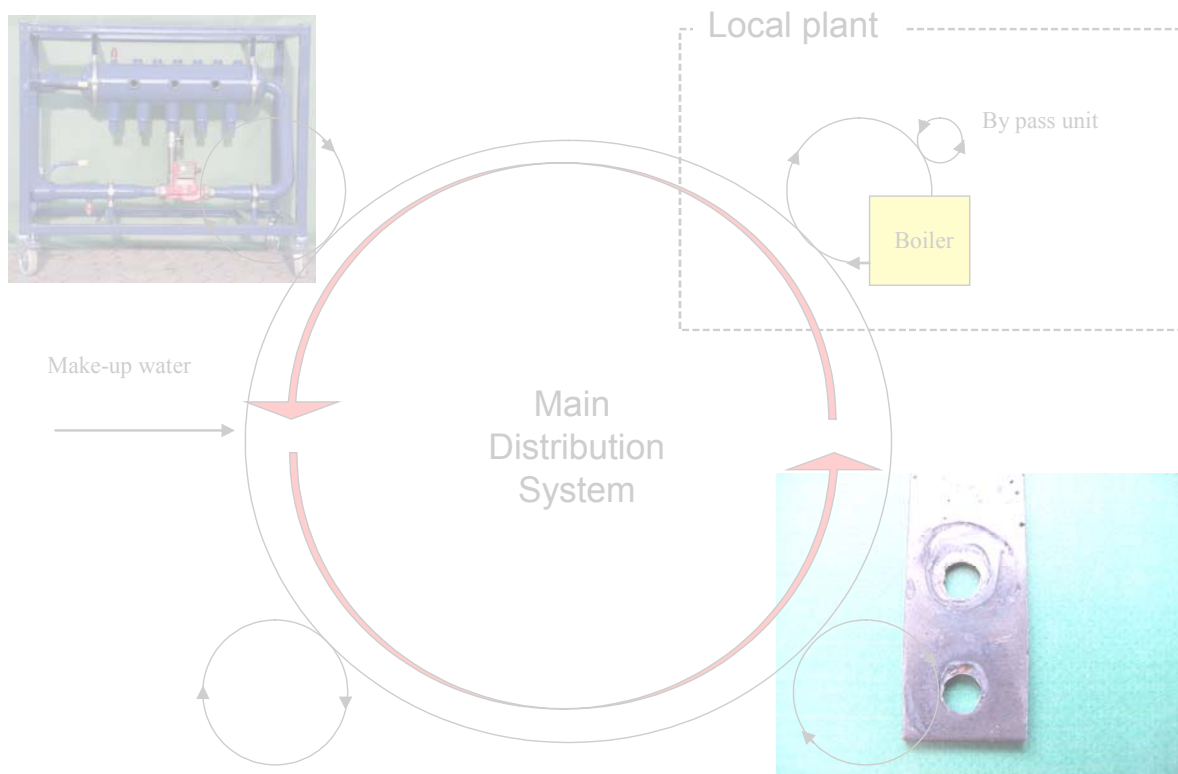
Danish participants:

Force Technology (project management)

MetriCorr

Technical University of Denmark

Measurements sampled over the period from 9 March 2003 to 1 March 2004.



Summary and conclusions

In connection with the joint Nordic project *Corrosion monitoring in district heating systems* corrosion measurements in circulating water from Aalborg distributing system were sampled over the period from 9 March 2003 till 1 March 2004. The measurements were made on a by-pass unit mounted at the decentralised works at Svendborgvej. Corrosion was determined on injected weight loss coupons, and over a limited period of time (9 April to 30 April 2003) the measuring program was intensified by performing concurrent environmental parameter measurements (pH, oxygen and conductivity) and measurements of the instantaneous corrosion rate at a number of contending on-line methods. The On-line methods' responses were compared to variations of the measured environmental parameters. Furthermore, the on-line methods' reliability during usual operation was compared to results from the injected weight loss coupons. Unfortunately the circulation through the by-pass unit was interrupted during the period from June 2003 to January 2004 and the particular influence on the coupon weight loss is not known. During the period when the by-pass unit was disrupted it was filled with pressurised water.

The overall result for all works is that highly sensitive ER (electric resistance) measurements is suitable for surveillance of general corrosion velocity and the LOCOR cell (crevice corrosion current) is suitable for surveillance of local corrosion risks. Both techniques have reacted fast to environmental changes in the systems and make possible continuous corrosion monitoring.

Highly sensitive ER may be interpreted as electronic weight loss measurements that on-line trace continuous variations in corrosion velocity over very short periods (hours). In comparison, credible weight loss measurements in such systems have required a measuring period of minimum 6 months.

Changes in crevice corrosion current measured with the LOCOR cell have clearly indicated presence of local corrosion but the final value of the current can only carefully be converted to corrosion velocity due to the localised character. The LOCOR cell gives response to changes in the risk of local corrosion within minutes and the results can thus be compared directly to changes in operation.

Two electrochemical methods – linearly polarisation measuring (LPM) and electrochemical impedance spectroscopy (EIS) – have been applied primarily for mechanism studies. The LPR method is used for commercial continuous corruptions surveillance/detection, but it is not recommendable in district heating systems, as it has resulted in a strong tendency to overrate the corrosion velocity. In general, the EIS method has resulted in more credible corrosion velocities but analysing the data is demanding and the measuring period is too long (several days) to register sudden changes.

As regards the on-going corrosion situation at the works is should be stressed and concluded that the make-up water then was very corrosive as corrosion velocities at as much as 1 mm/per year could be found. During normal operation it is indicated from the weight loss coupons that the corrosion velocity is at approximately 2 micrometer a year, which is as close to zero as it can get. Corrosion on the weight loss coupons was evenly distributed and no pitting was seen. As both the LOCOR cell and the ER measurements during normal operation showed very low corrosion velocities (<2 $\mu\text{m}/\text{year}$) it seems reasonable that the general corrosion velocity during normal operation is close to zero.

Background

System: The system is a distribution system with approximately 1200 km pipeline network. CEH and JC estimate a total volume of approximately 100.000 m³ of pipeline network. The heat is supplied by Nordjyllandsværket, Aalborg Portland and Reno Nord (waste incineration). The flow temperature in the period from week 19 to week 40 was 75 °C. From week 41 to week 18 the temperature is maintained between 80 °C and 92 °C at request. The return flow temperature is typically between 37 °C and 41 °C. The current network is made for operating pressures at 6,5 bar (Hence the requirement for the consumers' installation). Aalborg District Heating system guarantees differential pressures at 0,5 bar. It was noted that maintaining suitable operating pressures might be difficult in certain parts of the city because of altitude variations and pressure loss. The major part of the consumers, approximately 80-90% is connected directly to the system.

Make-up water: The make-up water consumption is approximately 550 m³/24 hours (23 m³/hour). Until recently make-up water has been supplied by Nordkraft (Aalborg midtby) but make-up water is now supplied by Nordjyllandsværket. Until recently, totally desalted water has been used, however, now RO-water from a new system (09-2001) is being used. The make-up water is deaerated in a vacuum deaerator before being dosed. Make-up water dosing is performed centrally in two 25.000 m³ accumulator tanks with a steam pillow. The accumulator tanks are placed at Nordjyllandsværket. Make-up water checks are performed at Nordjyllandsværket.

Circulating water: The oxygen content has previously been measured by the works to be 0 – 10 µg/l and the conductivity is from 35 – 45 µS/cm. The system is supplied with partial current cleansing. No oxygen absorbers or other additives are used. The pH-value is regulated at the Nordjyllandsværket with sodium hydroxide (lye).

Experience with corrosion and damages on the distribution network: No experience with inside corrosion.

Test program

Test conditions and placing of bypass-unit: Online corrosion measurements have been performed by the bypass-unit, Fig. 1b, attached to the distribution system at Svendborgvej heating central. Svendborgvej heating central is located in an area of the distribution net that can be regarded as an individually circulating system. The water in this part of the system is in hydraulic contact with the remaining system; but especially over the summer it is suspected that the water in the area is not being replaced or changed. Reno Nord is situated in this part of the system, and for a great part of the year is able to supply the whole area with the necessary heating. Svendborgvej Heating central has no make-up water dosing.

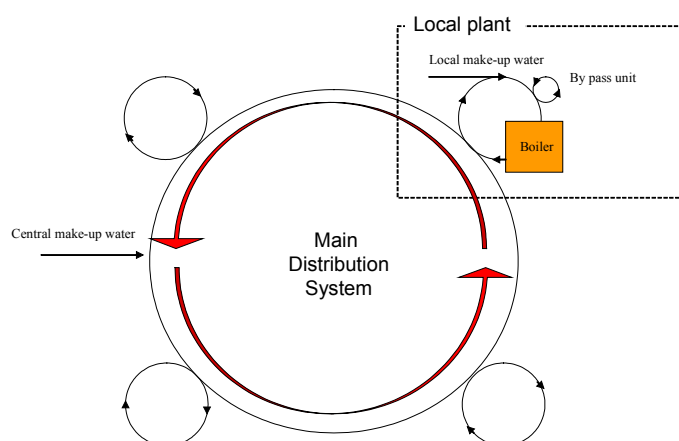


Figure 1a. Schematic presentation of the bypass-unit's location. Pipeline network at Aalborg.



Figure 1b. Photo of bypass-unit with circulation pump before probe mountings.

Corrosion measurements have been made with 5 methods, to which has been applied a total of 4 different probe types: Weight loss coupons, ER-probes, LOCOR-CELL and three electrodes for LPR and EIS measurements. Measurements have been performed in the bypass units measuring chamber, where it is possible to mount probes, both at the bottom, the side and the top. Probes mounted at the bottom of the measuring chamber are partly sheltered from the water flow, see Figure 2.

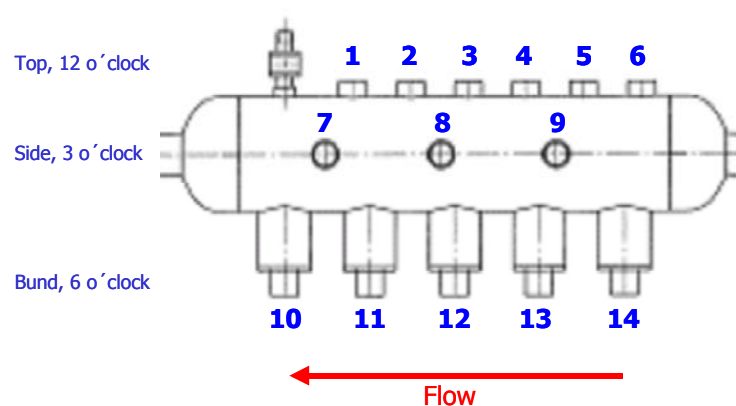


Figure 2. Probe locations in bypass-unit.

- 1: Weight loss coupon including steel disc for biofilm analysis
- 2: Empty
- 3: Three- electrode.
- 4: ER-probe
- 5: Weight loss coupon including steel disc for biofilm analysis
- 6: Weight loss coupon including steel disc for biofilm analysis
- 7: LOCOR-CELL
- 8: Thermo sensor
- 9: Empty
- 10: Weight loss coupon including steel disc for biofilm analysis
- 11: ER-probe with simulated deposits/crevice
- 12: Weight loss coupon including steel disc for biofilm analysis mounted in an extended bottom branch piece for simulation of a dead end
- 13: Three electrode
- 14: ER-probe.

Online measuring of water parameters (pH, conductivity and oxygen content) has been measured in a separate measuring panel, Figure 3, on an individual stream taken from the bypass-unit. Prior to measuring water parameters the individual stream is cooled in a sample cooler.

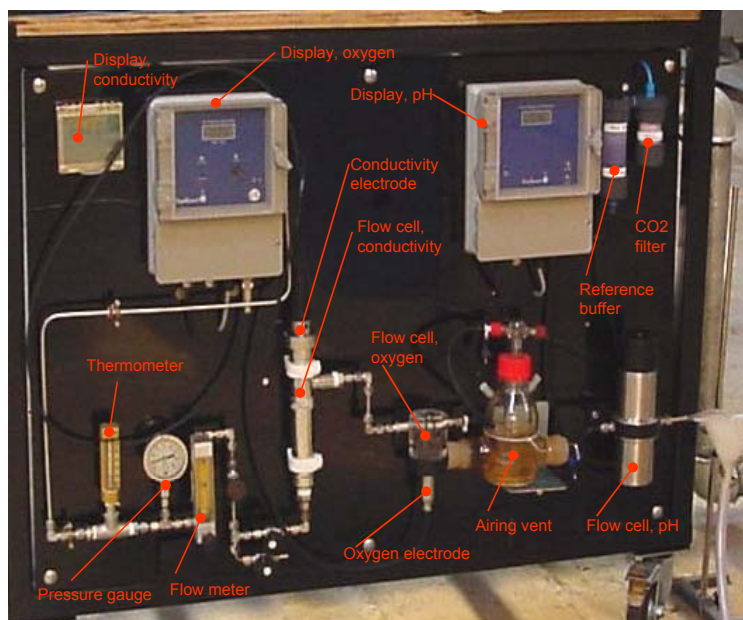


Figure 3. Photo of separate measuring panel for measuring water parameters.

All measurements (weight loss coupons excepted) are gathered on-line in a data logger. The Measurements can be traced centrally and at sight they may be included in the works' usual electronic surveillance.

Measuring results

Measuring results have been reproduced schematically below and are shown in curves in appendices 1-3. Photos of weight loss coupons are depicted in appendix 4.

During the entire testing period the environment is very stable and with the high pH, low oxygen and low conductivity no corrosion should occur, which is confirmed by the ER measurements and the LOCORCell, which gives very low rates. In this system it was not possible to conduct EIS measurements, and the performed LPR measurements give heavy overestimation of the corrosion rates. The LPR measurements gave linearly curves and should therefore be considered credible. The three-electrode probes were mat and uniformly dark. The system is thus regarded as stable and with subsequent low corrosion rates, but due to the stable environment it has not been possible to estimate the effect of any such unbalances in the environment.

Table 1. Schematic overview of measuring results.

Parameter	Measuring period	Normal operation
	Diurnal no.	0-20
Temperature, °C	0-20	35-41
Conductivity, $\mu\text{S}/\text{cm}$	0-20	43-47
pH	0-20	9,6-9,8
Oxygen, ppb	0-20	3-5
ER, $\mu\text{m}/\text{year}$, probe 4, top	0-14	0,8
ER, $\mu\text{m}/\text{year}$, probe 11, bottom	0-14	1,7
ER, $\mu\text{m}/\text{year}$, probe 14, bottom	14	0,9
LOCOR-Cell, $\mu\text{m}/\text{year}$, Probe 7 – 3 o'clock.	14-20	0
LPR, $\mu\text{m}/\text{year}$, probe 3, top	0	9,5
LPR, $\mu\text{m}/\text{year}$, probe 13, bottom	0	21
LPR, $\mu\text{m}/\text{year}$, probe 4, top	0	43
EIS, $\mu\text{m}/\text{year}$, probe 3, top	-	-
EIS, $\mu\text{m}/\text{year}$, probe 13, bottom	-	-
Weight loss, $\mu\text{m}/\text{year}$, probe 5, top	0-358	2
Weight loss, $\mu\text{m}/\text{year}$, probe 6, top	0-358	2
Weight loss, $\mu\text{m}/\text{year}$, probe 10, bottom	0-358	2

Table 2. Events during the test period.

Event no.	Description
0	Unit mounted on 09-03-2003
1	Online measurements started 09-04-2003 at 14:00
2	Online measurements terminated at 30-04-2003
3	Weight loss coupons drawn at 01-03-2004

Appendix 1. Measurements of water parameters

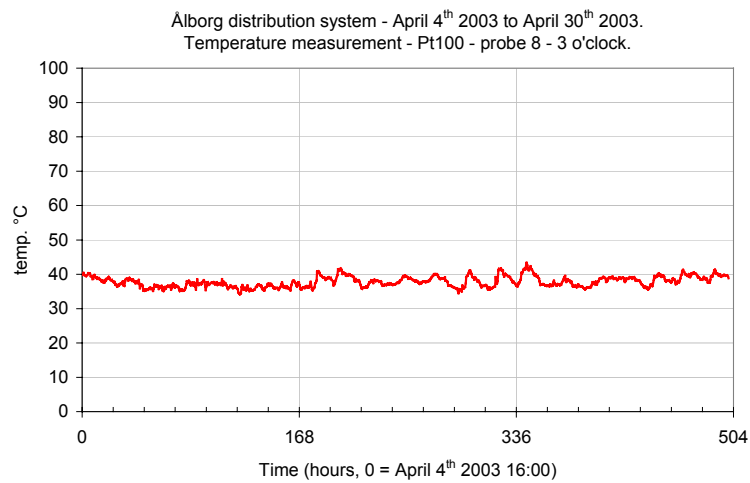


Figure 1. Circulating water temperature measured in the bypass-unit. Probe 8 – 3 o'clock.

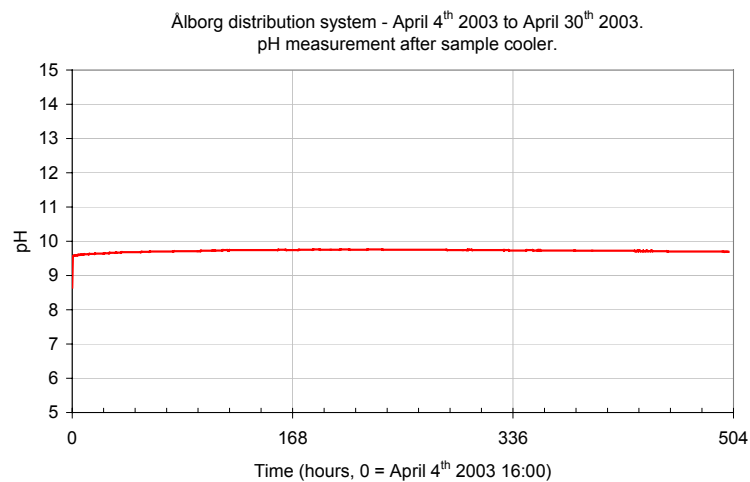


Figure 2. Circulating water pH-value measured in separate measuring panel after sample cooler.

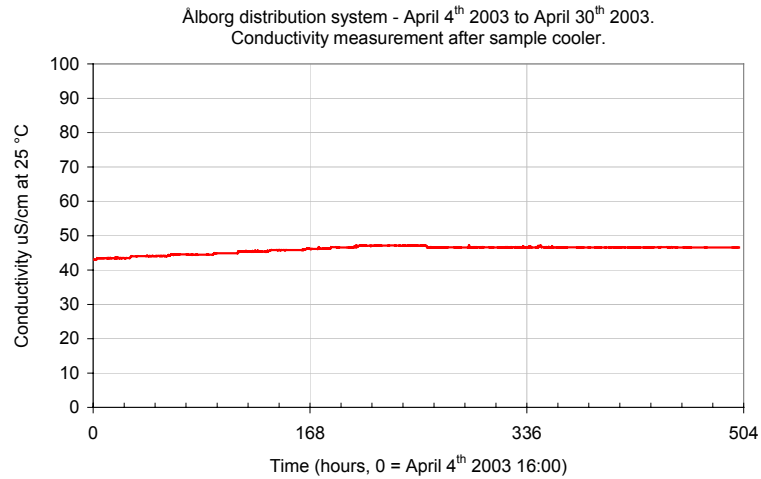


Figure 3. Circulating water conductivity measured in separate measuring panel after sample cooler.

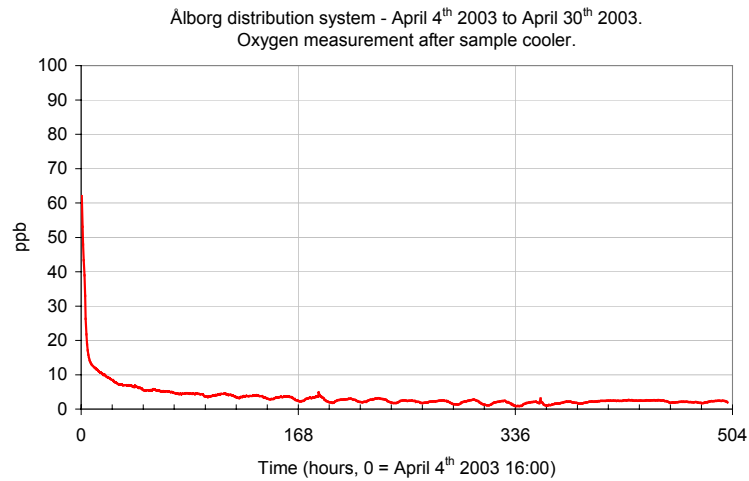


Figure 4. Circulating water oxygen content measured in separate measuring panel after sample cooler.

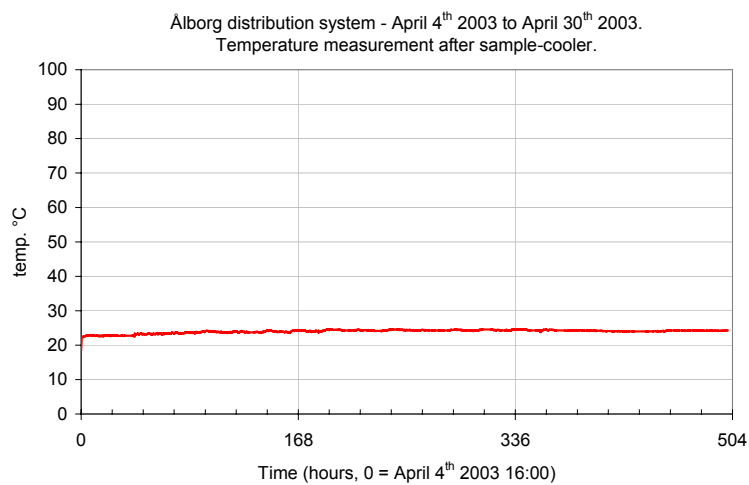


Figure 5. Temperature after sample cooler.

Appendix 2.

Corrosions measurements with ER-probes and LOCOR-CELL

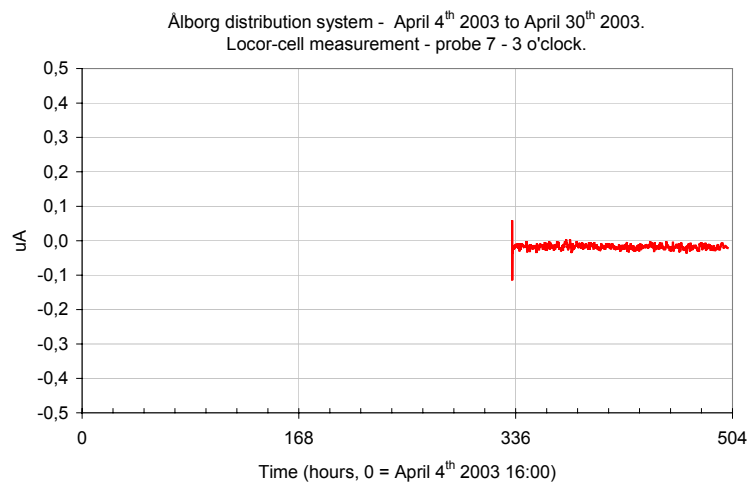


Figure 1. Measurements with the LOCOR-CELL. Probe 7 – 3 o'clock.

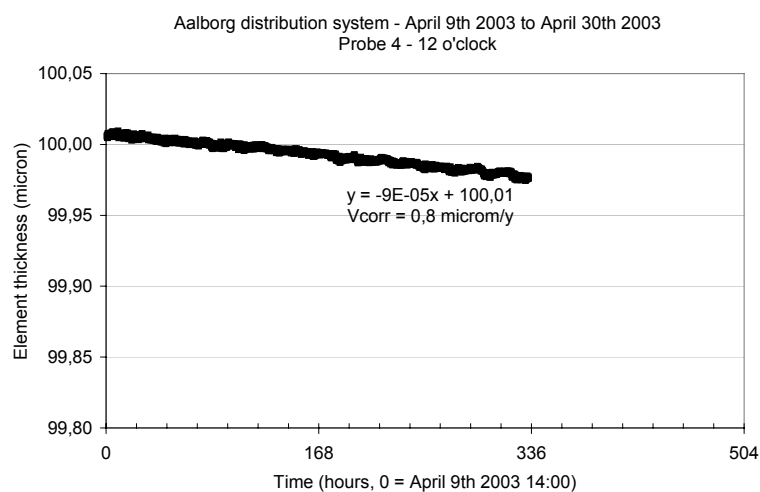


Figure 2. Measurements with ER-probe. Probe 4 – 12 o'clock.

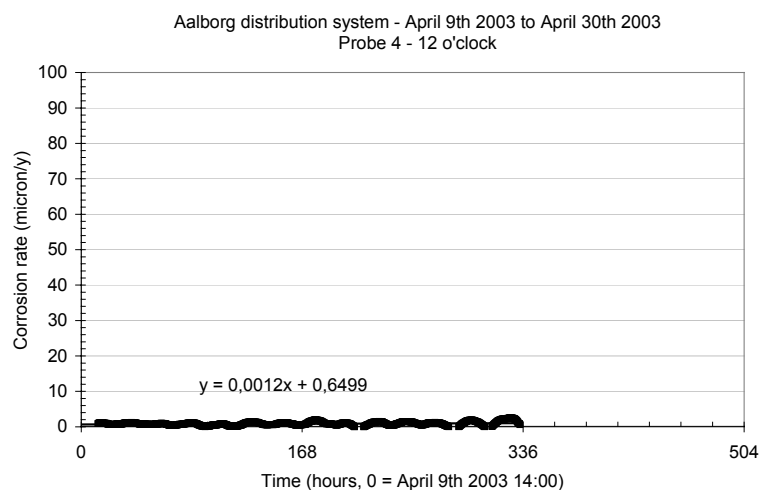


Figure 3. Measurements with ER-probe. Probe 4 – 12 o'clock.

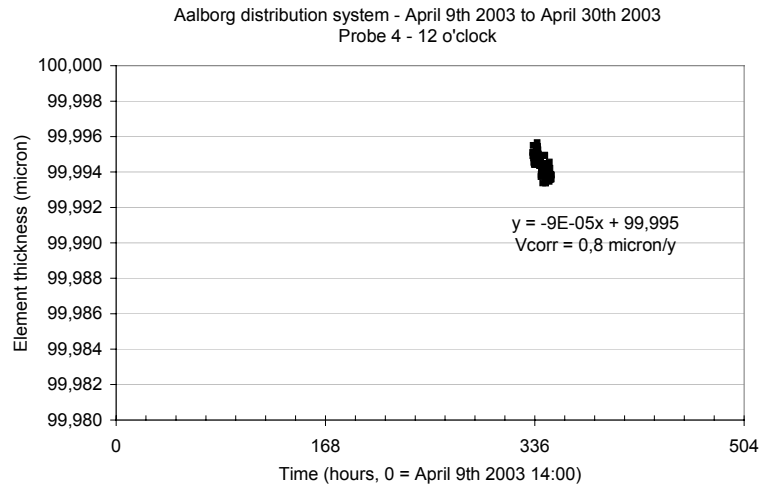


Figure 4. Measurements with ER-probe. Probe 4 – 12 o'clock.

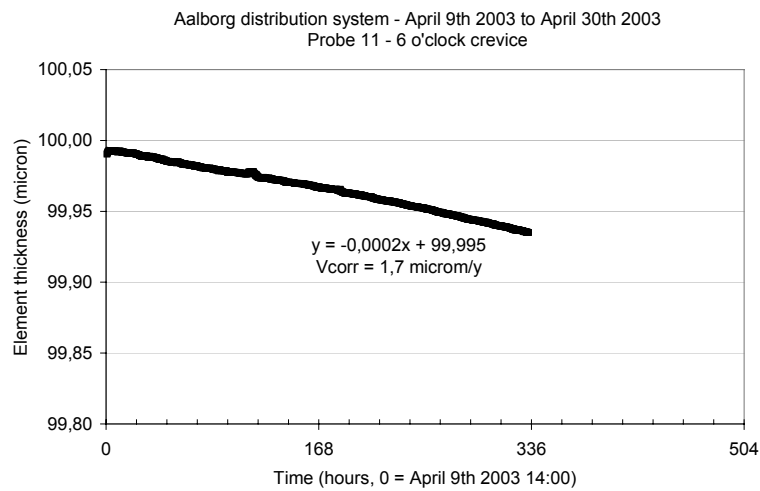


Figure 5. Measurements with covered ER-probe. Probe 11 – 6 o'clock.

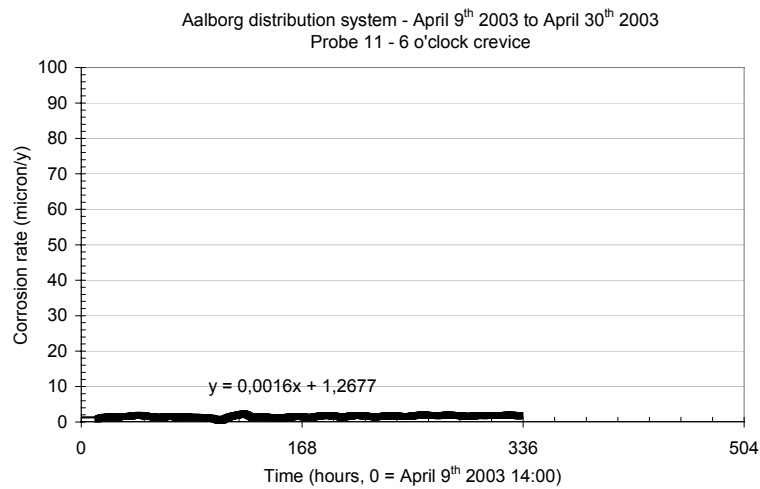


Figure 6. Measurements with covered ER-probe. Probe 11 – 6 o'clock.

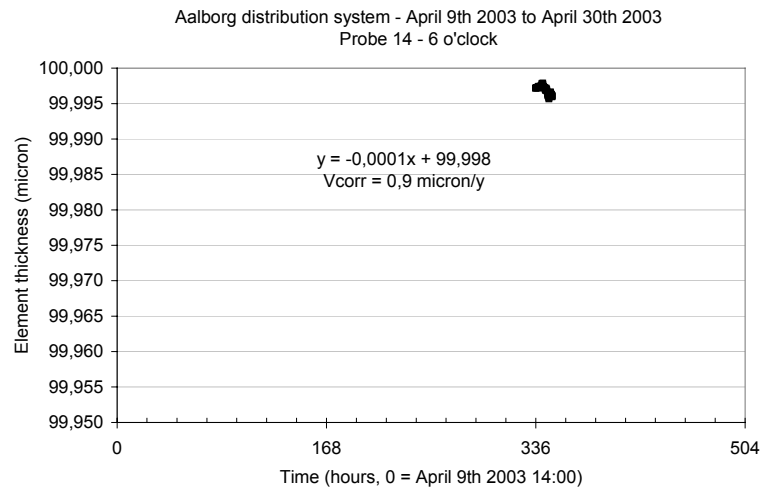


Figure 7. Measurements with covered ER-probe. Probe 14 – 6 o'clock.

Appendix 3. Corrosion measurements with three-electrodes LPR and EIS

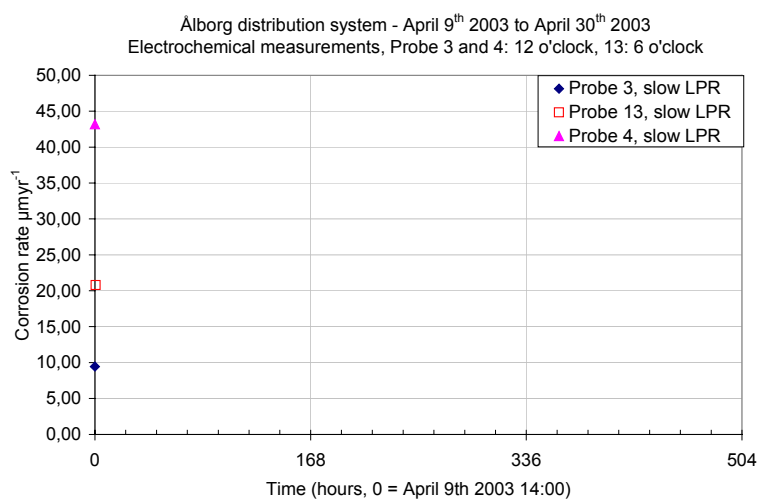


Figure 1. Probe 3 and 4 – 12 o'clock and Probe 13 – 6 o'clock.

Weight loss coupons.

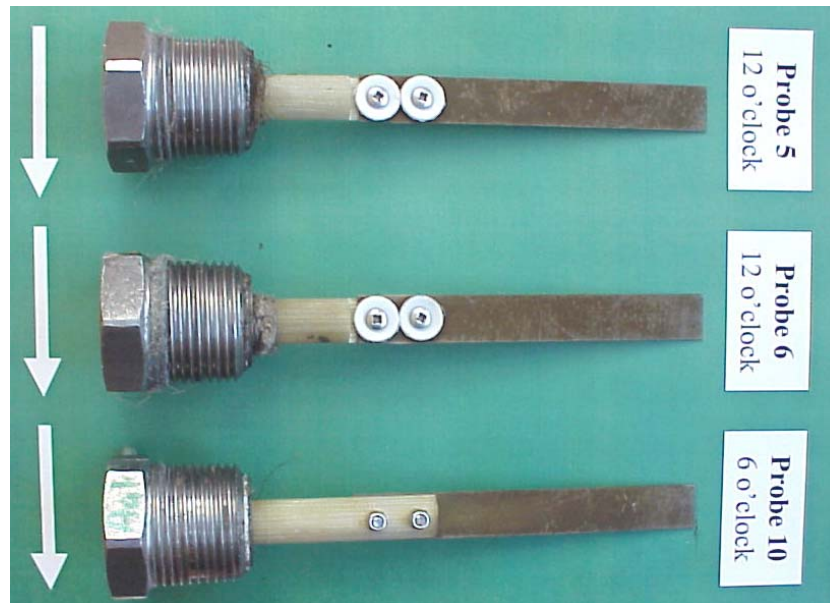


Photo 1. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

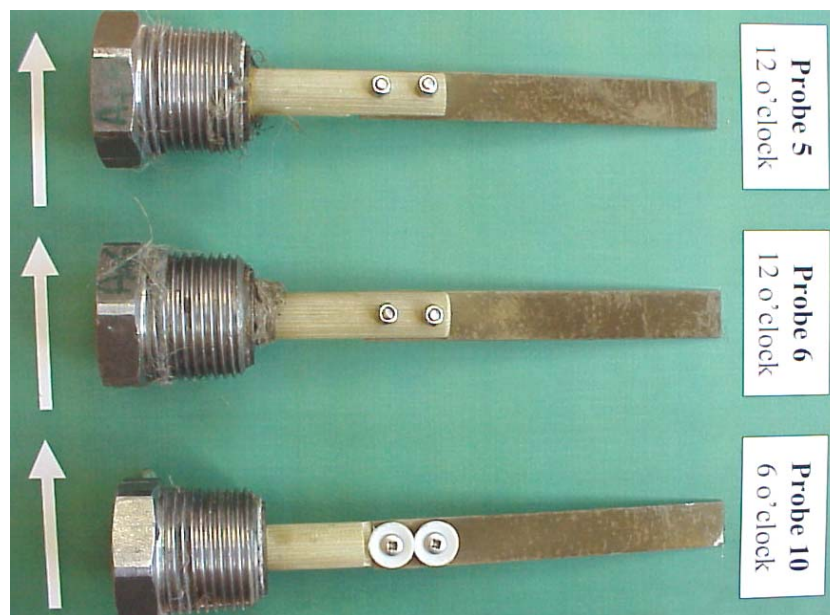


Photo 2. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

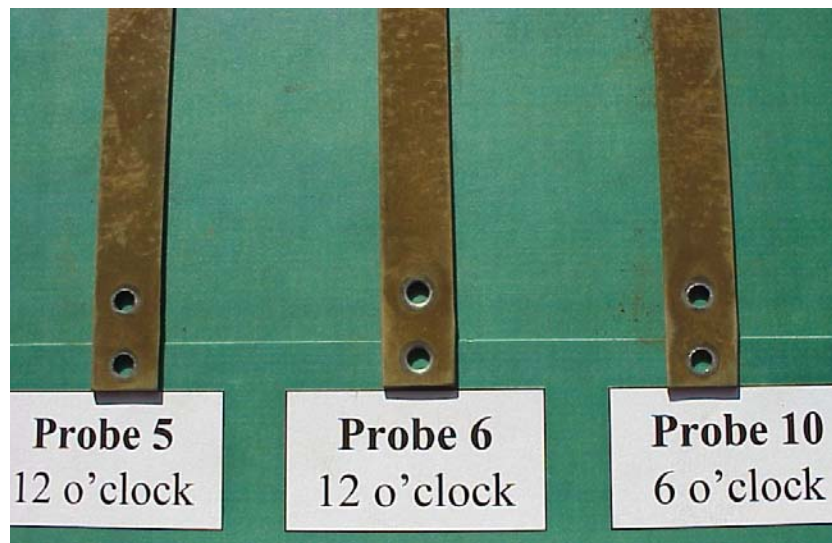


Photo 3. Detail of weight loss coupons. Seen from the left side, probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

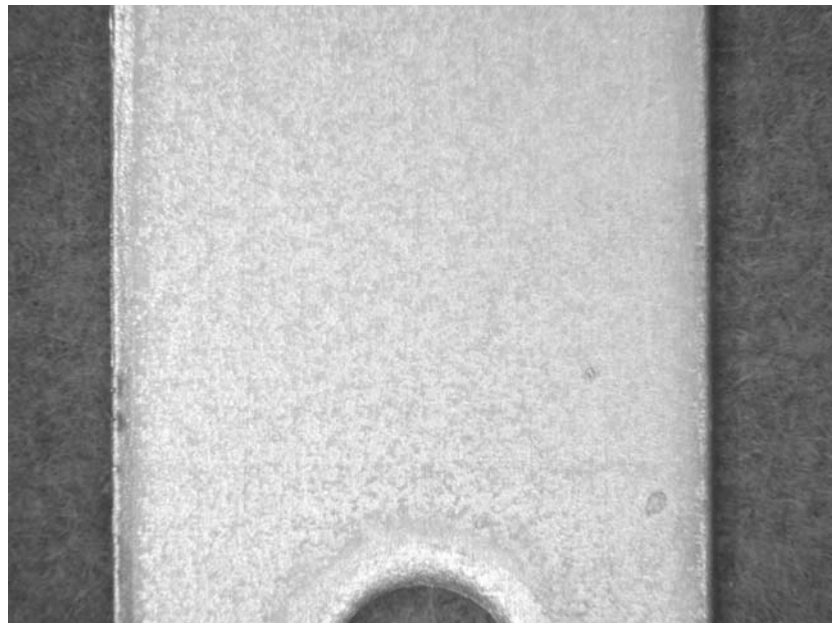


Photo 4. Detail of weight loss coupon probe 10 - 6 o'clock after cleaning. Approximately 6x enlargement.

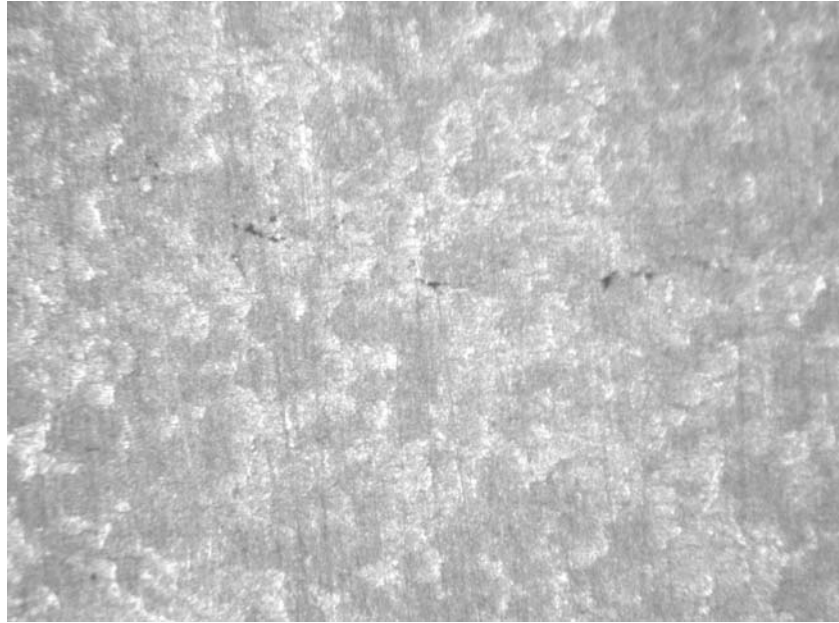


Photo 5. Detail of weight loss coupon probe 10 - 6 o'clock after cleaning. Approximately 50x enlargement.

Measuring report from Lundbeck cooling system

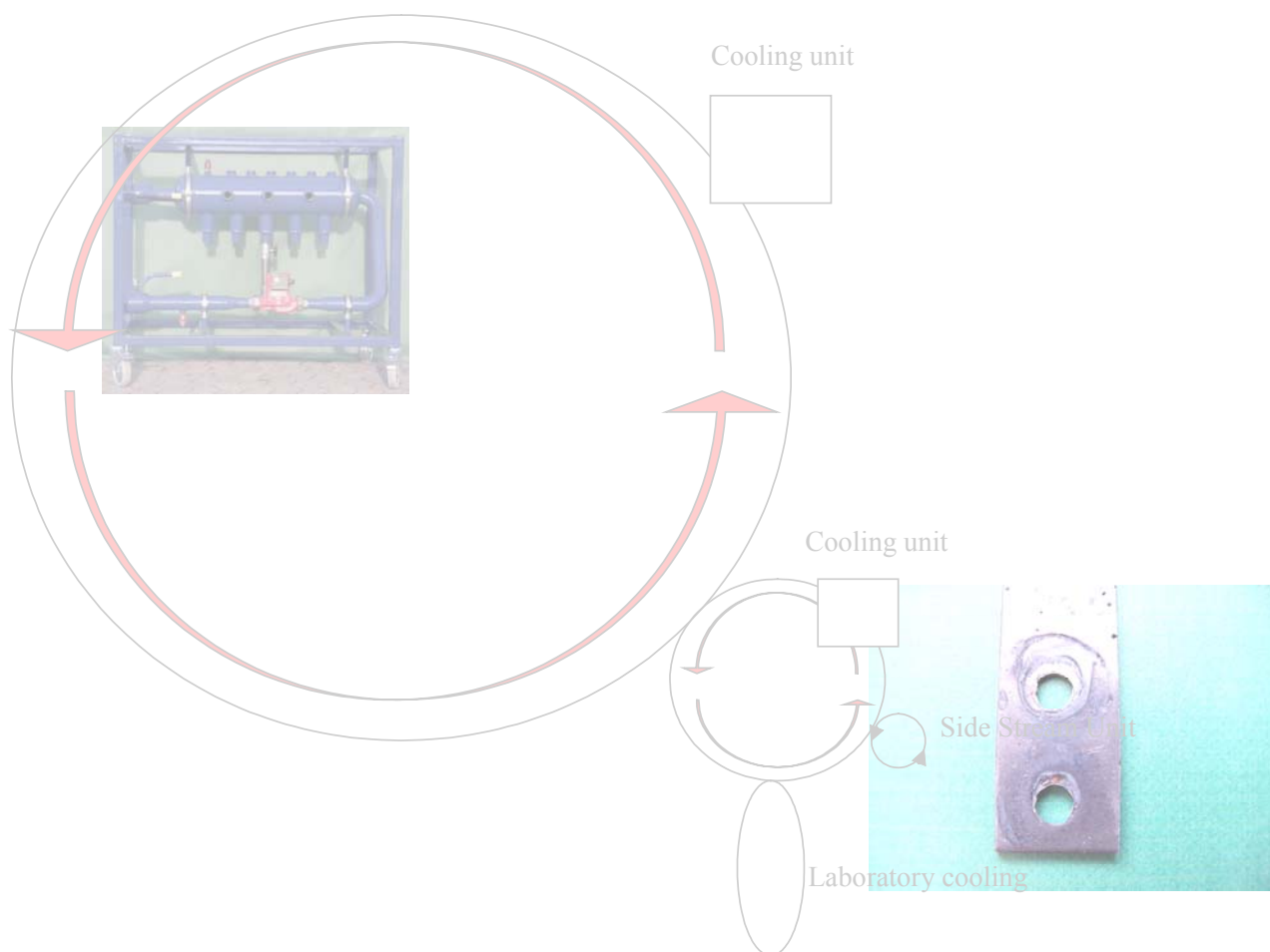
Monitoring of corrosion in district heating systems (KORMOF)

Joint Nordic project with support from Nordisk Industrifond (Nordic Innovation Centre)

Danish participants:

Force Technology (project management)
MetriCorr
Technical University of Denmark

Measurements sampled in the period from 14 October 2003 till 5 Marts 2004.



Summary and conclusions

In connection with the joint Nordic project *Corrosion monitoring in district heating systems* corrosion measurements in circulating water from Lundbeck cooling system were sampled over the period from 14 October 2003 till 5 Marts 2004. The measurements were made on a by-pass unit mounted at the return stream. Corrosion was determined on injected weight loss coupons, and through a limited period of time (21 October till 11 November 2003) the measuring program was intensified by performing concurrent environmental parameter measurements (pH, oxygen and conductivity) and measurements of the instantaneous corrosion rate at a number of contending on-line methods. The On-line methods' responses were compared to variations of the measured environmental parameters. Furthermore, the on-line methods' reliability during usual operation was compared to results from the injected weight loss coupons.

The overall result for all works is that highly sensitive ER (electric resistance) measurements is suitable for surveillance of general corrosion velocity and the LOCOR cell (crevice corrosion current) is suitable for surveillance of local corrosion risks. Both techniques have reacted fast to environmental changes in the systems and make possible continuous corrosion monitoring.

Highly sensitive ER may be interpreted as electronic weight loss measurements that on-line trace continuous variations in corrosion velocity over very short periods (hours). In comparison, credible weight loss measurements in such systems have required a measuring period of minimum 6 months.

Changes in crevice corrosion current measured with the LOCOR cell have clearly indicated presence of local corrosion but the final value of the current can only carefully be converted to corrosion velocity due to the localised character. The LOCOR cell gives response to changes in the risk of local corrosion within minutes and the results can thus be compared directly to changes in operation.

Two electrochemical methods – linearly polarisation measuring (LPM) and electrochemical impedance spectroscopy (EIS) – have been applied primarily for mechanism studies. The LPR method is used for commercial continuous corrossions surveillance/detection, but it is not recommendable in district heating systems, as it has resulted in a strong tendency to overrate the corrosion velocity. In general, the EIS method has resulted in more credible corrosion velocities but analysing the data is demanding and the measuring period is too long (several days) to register sudden changes.

As regards the on-going corrosion situation at the works is should be stressed and concluded that the environment was very stable during the intensified period of measurements. During normal operation it is indicated from the weight loss coupons that the average corrosion rate is negligible and it seems reasonable that the general corrosion rate during normal operation is close to zero. The relatively low pH and high conductivity increases the risk of corrosion damages during unintended oxygen ingress.

Background

System: The system is a relatively large closed and pressurised cooling system. The operating pressure is less than 6 bars at the return stream.

Make-up water: Make-up water was at the time of measurements untreated RO-water.

Circulating water: The oxygen content is stated as low (less than 20 ppb) and the conductivity between 330 and 350 $\mu\text{S}/\text{cm}$. The pH-value is stated as 8-9. The cooling system was initially filled with drinking water from Copenhagen.

Experience with corrosion and damages to the supply network. No experience with corrosion inside the pipes although particles in the circulating water has been a problem during the first years.

Test program

Location of bypass-unit: The bypass unit is mounted at the return stream after make-up water addition.

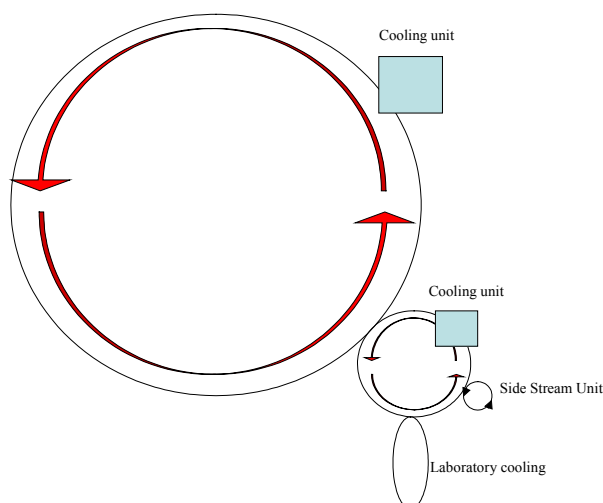


Figure 1a. Schematic presentation of the bypass-unit's location. At the time of measurements the large system was not yet connected to the smaller cooling system.



Figure 1b. Photo of bypass-unit with circulation pump before probe mountings.

Corrosion measurements have been made with 5 methods, to which has been applied a total of 4 different probe types: Weight loss coupons, ER-probes, LOCOR-CELL and three electrodes for LPR and EIS measurements. Measurements have been performed in the bypass units measuring chamber, where it is possible to mount probes, both at the bottom, the side and the top. Probes mounted at the bottom of the measuring chamber are partly sheltered from the water flow, see Figure 2.

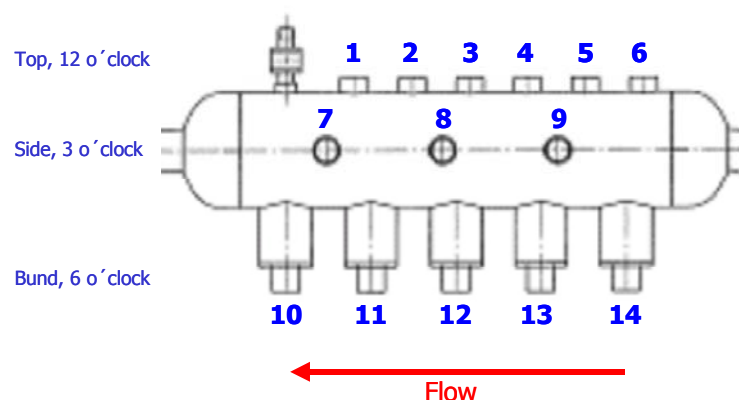


Figure 2. Probe locations in bypass-unit.

- 1: Weight loss coupon including steel disc for biofilm analysis
- 2: Empty
- 3: Three- electrode.
- 4: ER-probe
- 5: Weight loss coupon including steel disc for biofilm analysis
- 6: Weight loss coupon including steel disc for biofilm analysis
- 7: LOCOR-CELL
- 8: Thermo sensor
- 9: Empty
- 10: Weight loss coupon including steel disc for biofilm analysis
- 11: ER-probe with simulated deposits/crevice
- 12: Weight loss coupon including steel disc for biofilm analysis mounted in an extended bottom branch piece for simulation of a dead end
- 13: Three electrode
- 14: ER-probe.

Online measuring of water parameters (pH, conductivity and oxygen content) has been measured in a separate measuring panel, Figure 3, on an individual stream taken from the bypass-unit. Prior to measuring water parameters the individual stream is cooled in a sample cooler.

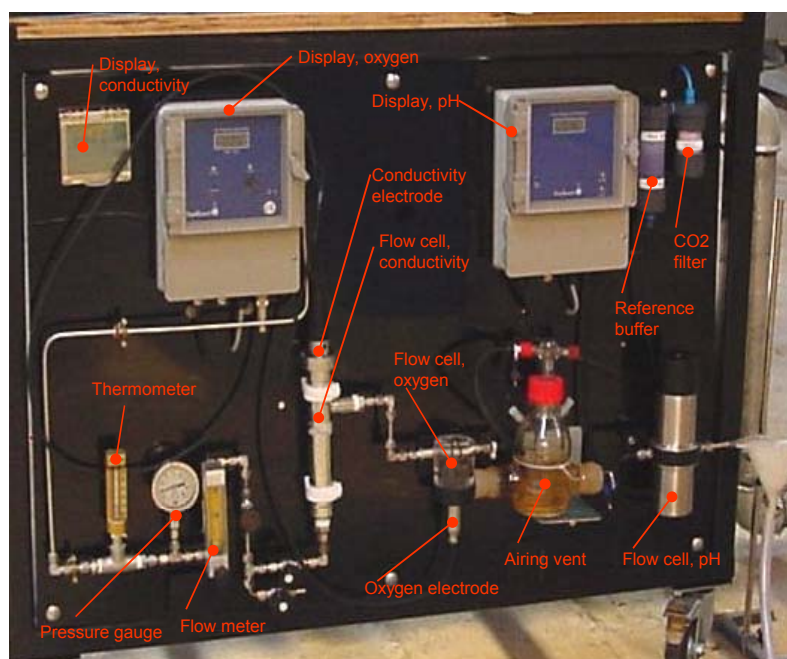


Figure 3. Separate measuring panel for measuring water parameters.

All measurements (weight loss coupons excepted) are gathered on-line in a data logger. The Measurements can be traced centrally and at sight they may be included in the works' usual electronic surveillance.

Measuring results

Measuring results have been reproduced schematically below and are shown in curves in appendices 1-3. Photos of weight loss coupons are shown in appendix 4.

During the intensified measuring period the environment was stable and the corrosion rate negligible. This is confirmed from the ER-probes and the LOCOR cell. LPR and EIS measurements correlate with the measurements from ER and LOCOR cell. The system must be considered stable with low corrosion rates although effects of changes in the environment cannot be assessed due to the stable environment during measurements. The relatively low pH and high conductivity increases the risk of corrosion damages during unintended oxygen ingress.

Table 1. Schematic overview of measuring results.

Parameter	Measuring period	Normal operation
	Day + night no.	0-22
Temperature, °C	0-21	6,5-7,5
Conductivity $\mu\text{S}/\text{cm}$	0-21	330-350
PH	0-21	8,8-8,9
Oxygen, ppb	0-21	0
ER, $\mu\text{m}/\text{year}$, probe 4, top	0-20	0
ER, $\mu\text{m}/\text{year}$, probe 11, bottom	0-20	0,6
ER, $\mu\text{m}/\text{year}$, probe 14, bottom	0-20	0
LOCOR-Cell, Probe 7 – 3 o'clock.	0-21	0 ¹
LPR, $\mu\text{m}/\text{year}$, probe 3, top	7/21	0,4/0,4 ²
LPR, $\mu\text{m}/\text{year}$, probe 13, bund	3/7/13/21	0,6/0,7/0,4/1,1 ²
EIS, $\mu\text{m}/\text{year}$, probe 3, top	0/13	0,6/0,7
EIS, $\mu\text{m}/\text{year}$, probe 13, bund	3/13	0,7/0,5
Weight loss, $\mu\text{m}/\text{year}$, probe 5, top	143	<1 (0,4)
Weight loss, $\mu\text{m}/\text{year}$, probe 6, top	143	<1 (0,4)
Weight loss, $\mu\text{m}/\text{year}$, probe 10, bottom	143	<1 (0,5)

1: Small negative current.

2: Slow LPR.

Table 2. Events over the test period.

Event no.	Description
0	Unit mounted 14-10-2003
1	Online measurements started on 21-10-2003
2	Online measurements ended on 11-11-2003
3	Measurements ended 05-03-2004

Appendix 1. Measurements of water parameters

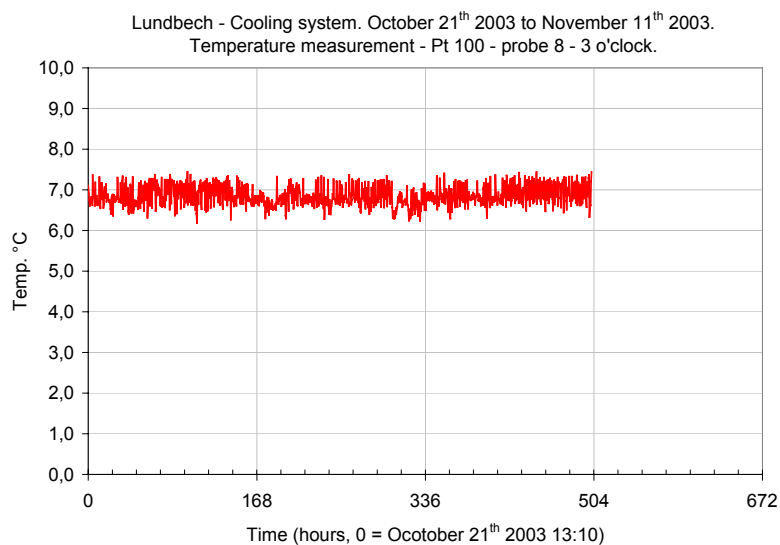


Figure 1. Circulating water temperature measured in the bypass unit. Probe 8 – 3 o'clock.

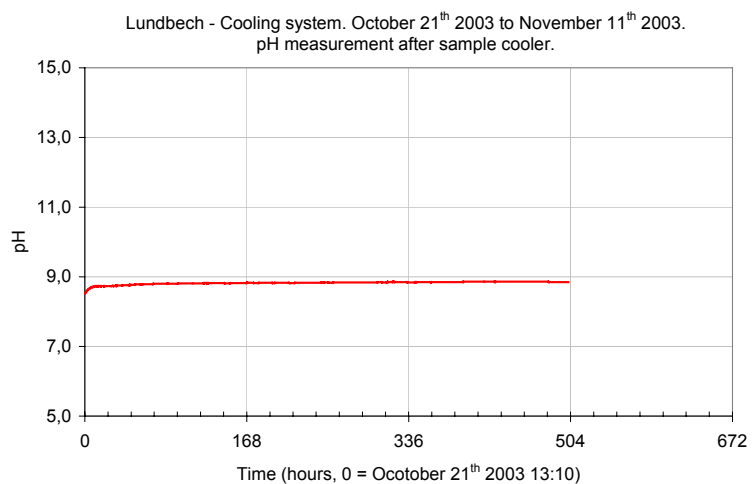


Figure 2. Circulating water pH-value measured in separate measuring panel after sample cooler.

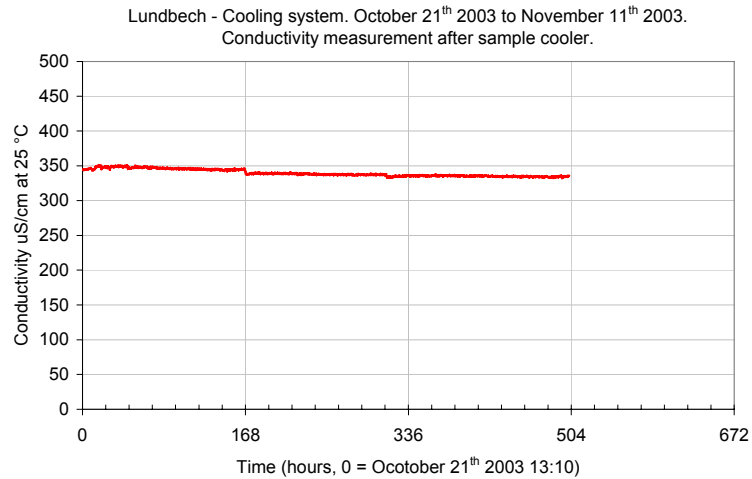


Figure 3. Circulating water conductivity measured in separate measuring panel after sample cooler.

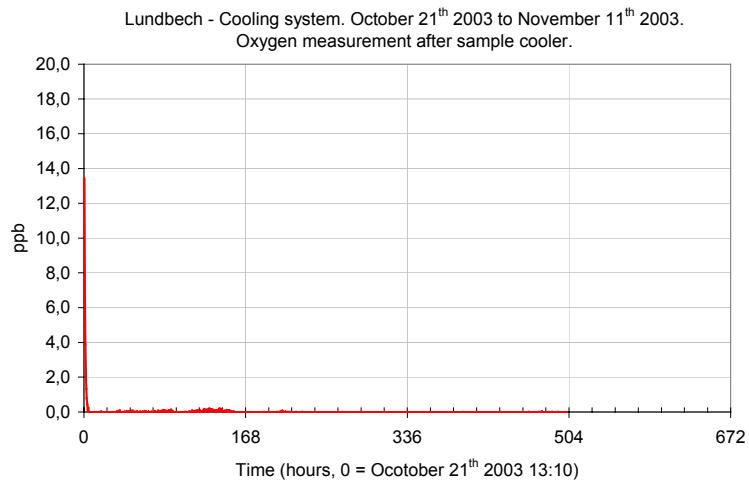


Figure 4. Circulating water oxygen content measured in separate measuring panel after sample cooler.

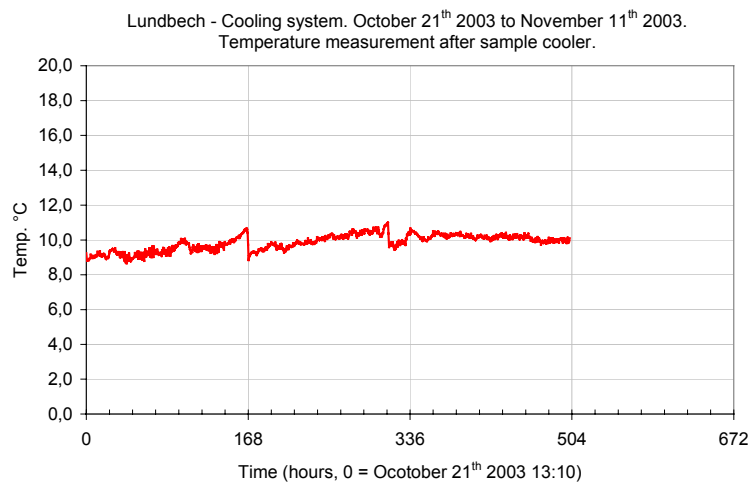


Figure 5. Temperature after sample cooler.

Appendix 2.

Corrosion measurements with ER-probes and LOCOR-CELL

Lundbech - Cooling system. October 21st 2003 to November 11th 2003.
Locor-cell measurement - probe 7 - 3 o'clock.

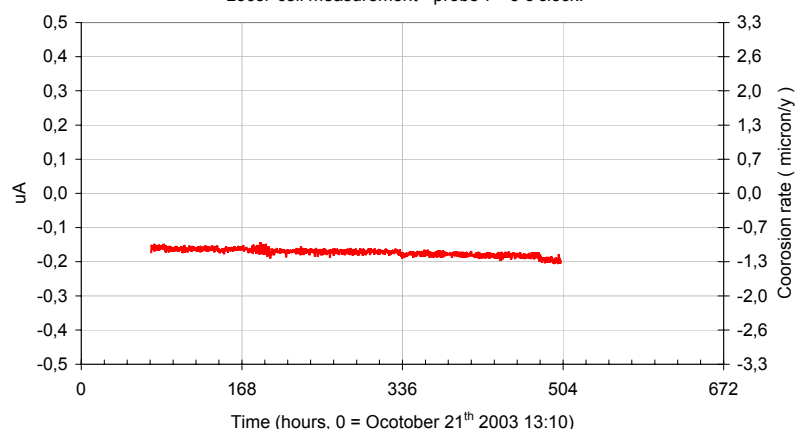


Figure 1. Measurements with the LOCOR-CELL. Probe 7 – 3 o'clock.
The measured corrosion rates shall be multiplied by a factor 5-10 to compensate for local corrosion attacks on the anode.

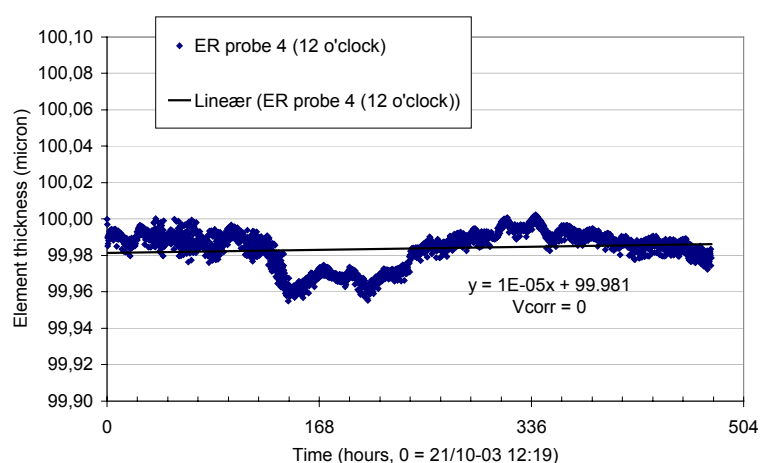


Figure 2. Measures with ER-probe. Probe 4 – 12 o'clock.

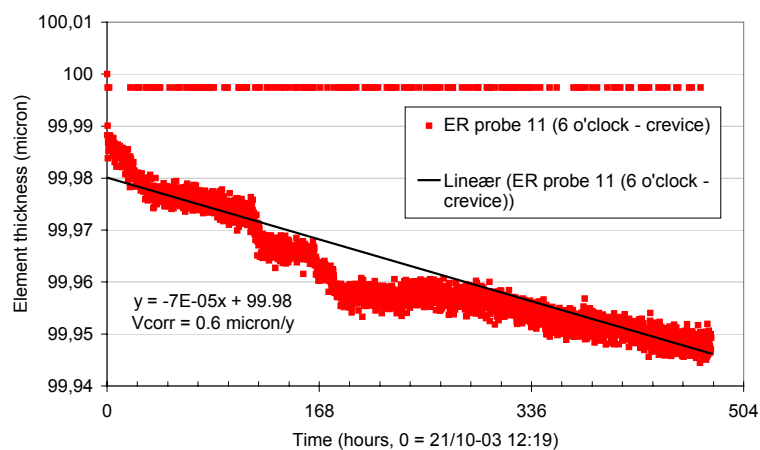


Figure 3. Measurements with covered ER-probe. Probe 11 – 6 o'clock.

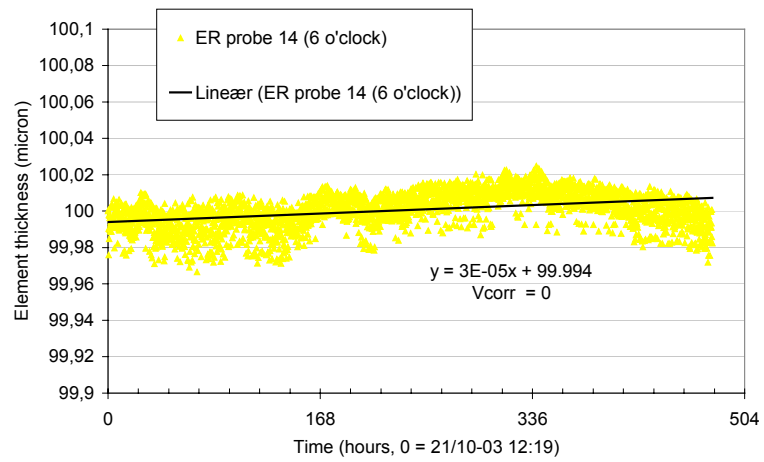


Figure 4. Measurements with ER-probe Probe 14 – 6 o'clock.

Appendix 3. Corrosion measures with three electrodes LPR and EIS

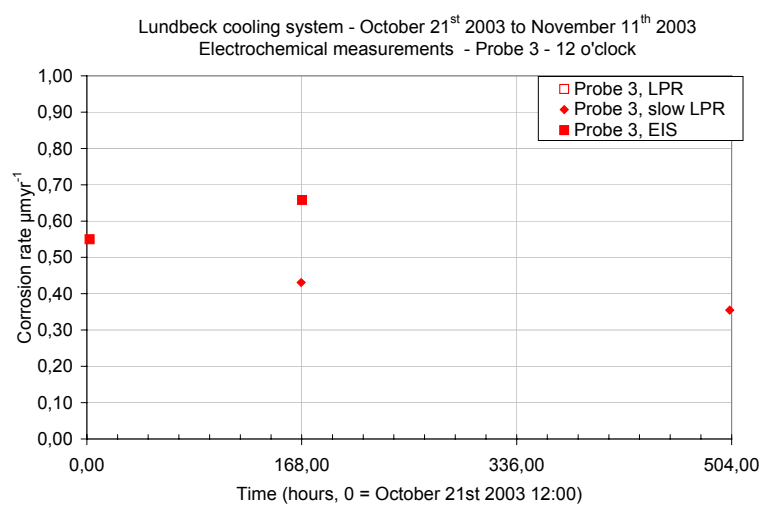


Figure 1. Probe 3 – 12 o'clock.

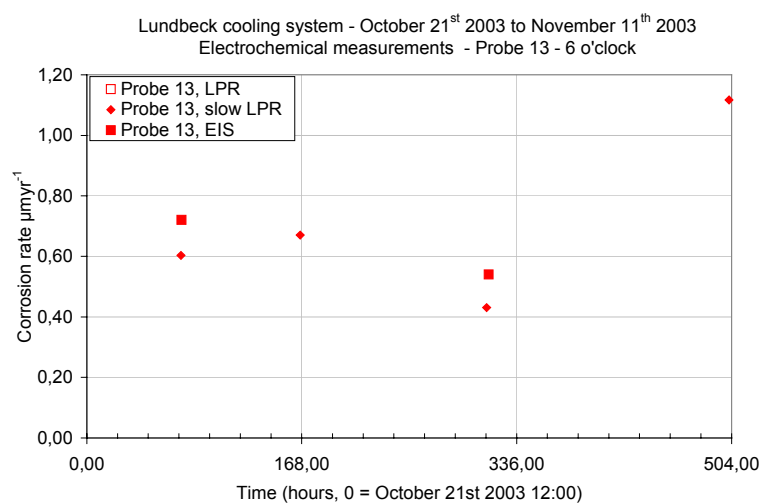


Figure 2. Probe 13 – 6 o'clock.

Weight loss coupons



Photo 1. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.



Photo 2. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

Measuring report from Lundbeck central heating system

Monitoring of corrosion in district heating systems (KORMOF)

Joint Nordic project with support from Nordisk Industrifond (Nordic Innovation Centre)

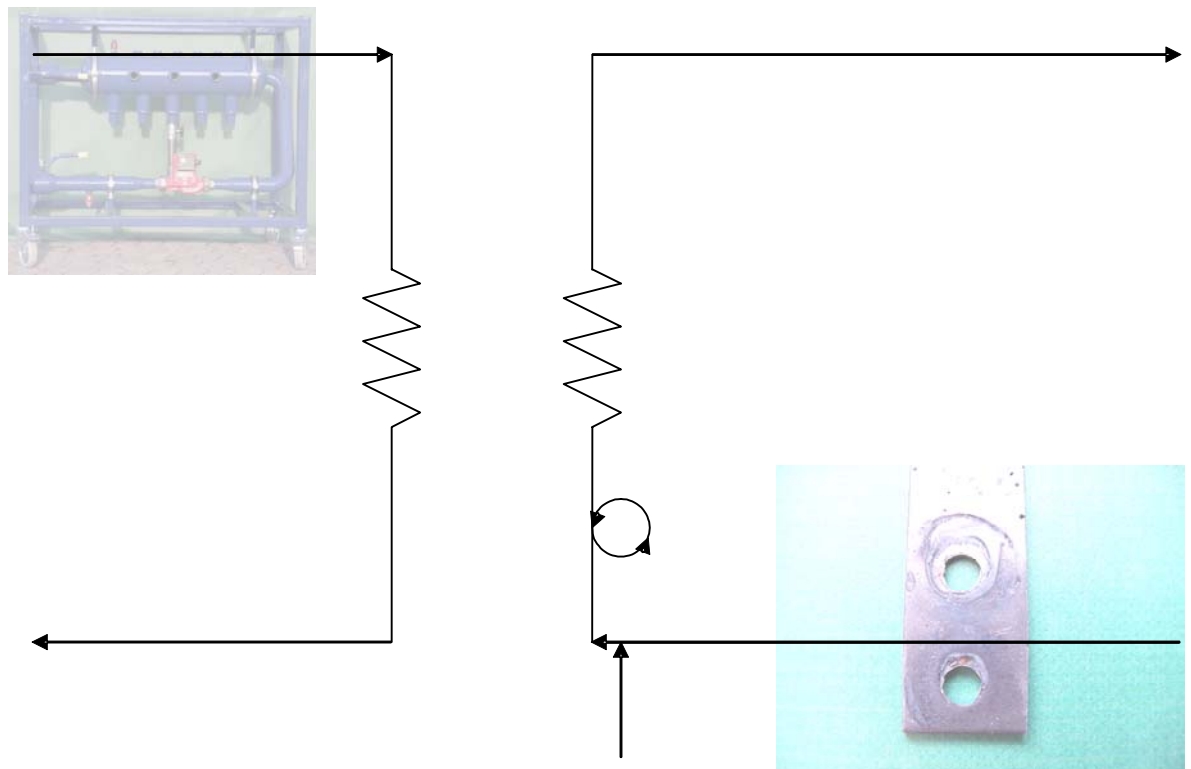
Danish participants:

Force Technology (project management)

MetriCorr

Technical University of Denmark

Measurements sampled in the period from 14 October 2003 till 5 Marts 2004.



Summary and conclusions

In connection with the joint Nordic project *Corrosion monitoring in district heating systems* corrosion measurements in circulating water from Lundbeck central heating system were sampled over the period from 14 October 2003 till 5 Marts 2004. The measurements were made on a by-pass unit mounted at the return stream. Corrosion was determined on injected weight loss coupons, and through a limited period of time (11 November till 9 December 2003) the measuring program was intensified by performing concurrent environmental parameter measurements (pH, oxygen and conductivity) and measurements of the instantaneous corrosion rate at a number of contending on-line methods. The On-line methods' responses were compared to variations of the measured environmental parameters. Furthermore, the on-line methods' reliability during usual operation was compared to results from the injected weight loss coupons. Unfortunately the water amount of water used to ensure measurements of pH, conductivity and oxygen led to a critical water loss from the central heating system and following automatic use of makeup water. Therefore the first week of intensified measurements does not match the normal conditions in the central heating system. The continuous measurements on water quality were ended after one week.

The overall result for all works is that highly sensitive ER (electric resistance) measurements is suitable for surveillance of general corrosion velocity and the LOCOR cell (crevice corrosion current) is suitable for surveillance of local corrosion risks. Both techniques have reacted fast to environmental changes in the systems and make possible continuous corrosion monitoring.

Highly sensitive ER may be interpreted as electronic weight loss measurements that on-line trace continuous variations in corrosion velocity over very short periods (hours). In comparison, credible weight loss measurements in such systems have required a measuring period of minimum 6 months.

Changes in crevice corrosion current measured with the LOCOR cell have clearly indicated presence of local corrosion but the final value of the current can only carefully be converted to corrosion velocity due to the localised character. The LOCOR cell gives response to changes in the risk of local corrosion within minutes and the results can thus be compared directly to changes in operation.

Two electrochemical methods – linearly polarisation measuring (LPM) and electrochemical impedance spectroscopy (EIS) – have been applied primarily for mechanism studies. The LPR method is used for commercial continuous corrossions surveillance/detection, but it is not recommendable in district heating systems, as it has resulted in a strong tendency to overrate the corrosion velocity. In general, the EIS method has resulted in more credible corrosion velocities but analysing the data is demanding and the measuring period is too long (several days) to register sudden changes.

As regards the on-going corrosion situation at the works is should be stressed that under normal operation without makeup water addition it seems reasonable that the general corrosion rate is close to zero. However during excessive use of makeup water corrosion rates of up to 80 $\mu\text{m}/\text{year}$ were observed on the ER probes and app. 20 $\mu\text{m}/\text{year}$ was observed in the LOCOR cell. Corrosion on the weight loss coupons was evenly distributed and no pitting was seen. The relatively high average corrosion rates found on the weight loss coupons (7-9 $\mu\text{m}/\text{year}$) are properly caused by the excessive makeup water addition in the first week of online measurements. The relatively low pH and high conductivity increases the risk of corrosion damages during unintended oxygen ingress.

Background

System: The system is a closed and pressurised central heating system. The operating pressure is less than 6 bars at the return stream.

Make-up water: Make-up water was at the time of measurements untreated drinking water.

Circulating water: The oxygen content is stated as low (less than 20 ppb) and the conductivity between 300 and 400 $\mu\text{S}/\text{cm}$. The pH-value is stated as 8-10.

Experience with corrosion and damages to the supply network. No experience with corrosion inside the pipes.

Test program

Location of bypass-unit: The bypass unit is mounted at the return stream after make-up water addition.

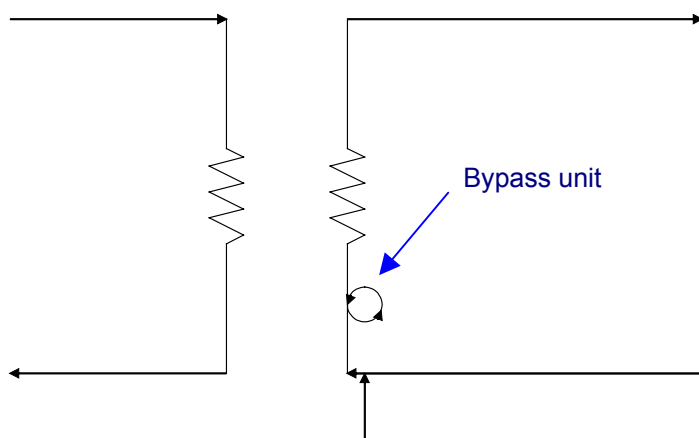


Figure 1a. Schematic presentation of the bypass-unit's location.



Figure 1b. Photo of bypass-unit with circulation pump before probe mountings.

Corrosion measurements have been made with 5 methods, to which has been applied a total of 4 different probe types: Weight loss coupons, ER-probes, LOCOR-CELL and three electrodes for LPR and EIS measurements. Measurements have been performed in the bypass units measuring chamber, where it is possible to mount probes, both at the bottom, the side and the top. Probes mounted at the bottom of the measuring chamber are partly sheltered from the water flow, see Figure 2.

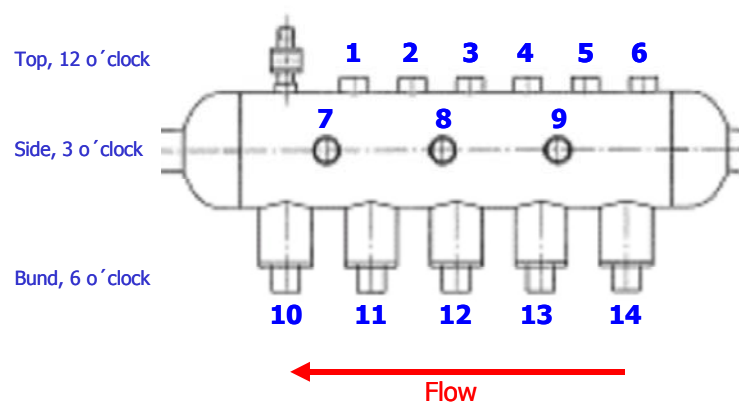


Figure 2. Probe locations in bypass-unit.

- 1: Weight loss coupon including steel disc for biofilm analysis
- 2: Empty
- 3: Three- electrode.
- 4: ER-probe
- 5: Weight loss coupon including steel disc for biofilm analysis
- 6: Weight loss coupon including steel disc for biofilm analysis
- 7: LOCOR-CELL
- 8: Thermo sensor
- 9: Empty
- 10: Weight loss coupon including steel disc for biofilm analysis
- 11: ER-probe with simulated deposits/crevice
- 12: Weight loss coupon including steel disc for biofilm analysis mounted in an extended bottom branch piece for simulation of a dead end
- 13: Three electrode
- 14: ER-probe.

Online measuring of water parameters (pH, conductivity and oxygen content) has been measured in a separate measuring panel, Figure 3, on an individual stream taken from the bypass-unit. Prior to measuring water parameters the individual stream is cooled in a sample cooler.

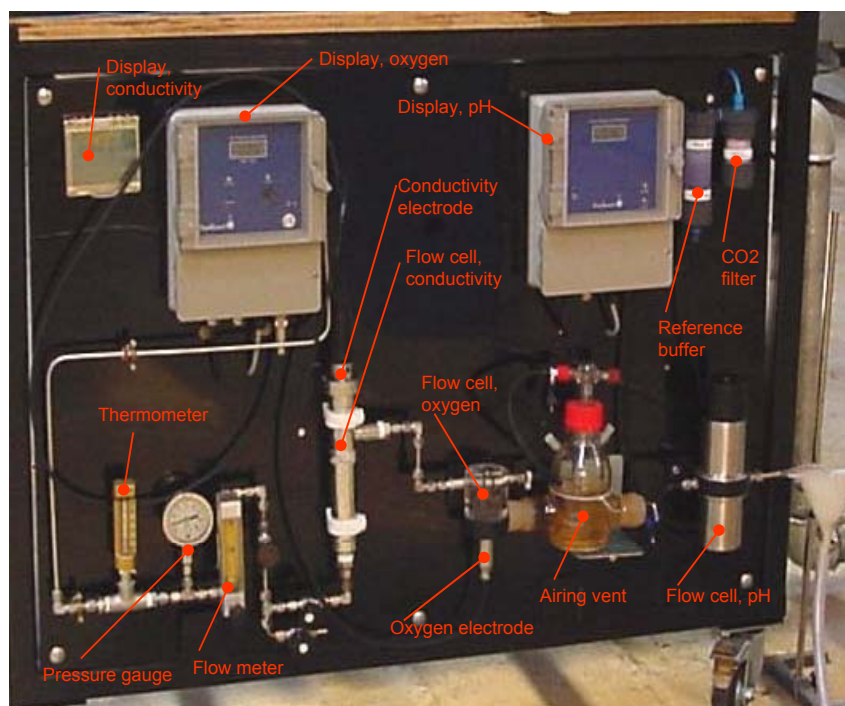


Figure 3. Photo of separate measuring panel for measuring water parameters.

All measurements (weight loss coupons excepted) are gathered on-line in a data logger. The Measurements can be traced centrally and at sight they may be included in the works' usual electronic surveillance.

Measuring results

Measuring results have been reproduced schematically below and are shown in curves in appendices 1-3. Photos of weight loss coupons are shown in appendix 4.

After the first week of the intensified measuring period the environment was stable and the corrosion rates low. This is confirmed from the ER-probes and the LOCOR cell. LPR and EIS measurements also confirm this but do in some extend overestimate corrosion rates. The system must be considered stable with low corrosion rates under normal operation. The system is very sensitive to relatively small losses of water that automatically leads to makeup eater addition. During the first week of online measurements ER and the LOCOR cell showed as expected considerably higher corrosion rates than under normal operation. The same was the case for EIS and LPR although the methods properly over estimate the corrosion rate during this period.

Table 1. Schematic overview of measuring results.

Parameter	Measuring period	Normal operation ¹
	Day + night no.	0-22
Temperature, °C	0-28	62-78 (45-70)
Conductivity $\mu\text{S}/\text{cm}$	0-28	330-360
PH	0-28	9
Oxygen, ppb	0-28	0 (>100)
ER, $\mu\text{m}/\text{year}$, probe 4, top	0-7	- (81)
ER, $\mu\text{m}/\text{year}$, probe 11, bottom	0-28	0 (>5)
ER, $\mu\text{m}/\text{år}$, probe 14, bottom	0-28	<17 (>17)
LOCOR-Cell, Probe 7 – 3 o'clock.	0-28	0 (18)
LPR, $\mu\text{m}/\text{year}$, probe 3, top	-	-
LPR, $\mu\text{m}/\text{year}$, probe 13, bund	3/28	251/14 ²
EIS, $\mu\text{m}/\text{year}$, probe 3, top	-	-
EIS, $\mu\text{m}/\text{year}$, probe 13, bund	3	200
Weight loss, $\mu\text{m}/\text{year}$, probe 5, top	143	8
Weight loss, $\mu\text{m}/\text{year}$, probe 6, top	143	9
Weight loss, $\mu\text{m}/\text{year}$, probe 10, bottom	143	7

1: Numbers in brackets are referring to the unstable period in the first week of measurements.

2: Slow LPR.

Table 2. Events over the test period.

Event no.	Description
0	Unit mounted 14-10-2003
1	Online measurements started on 21-10-2003
2	Online measurements ended on 11-11-2003
3	Measurements ended 05-03-2004

Appendix 1. Measurements of water parameters

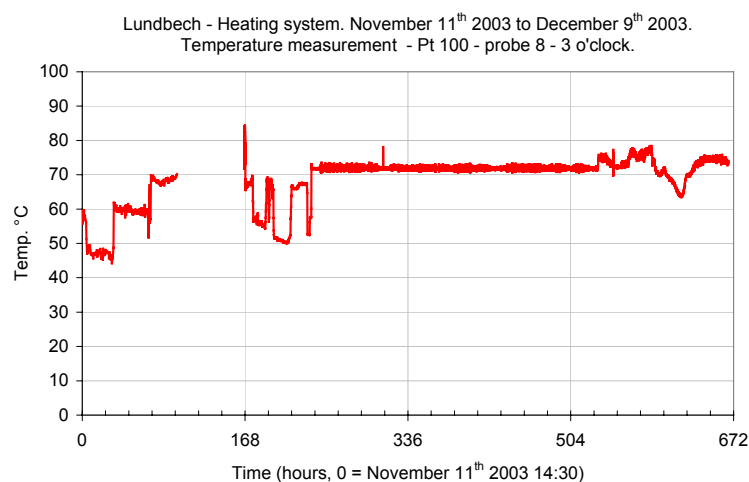


Figure 1. Circulating water temperature measured in the bypass unit. Probe 8 – 3 o'clock.

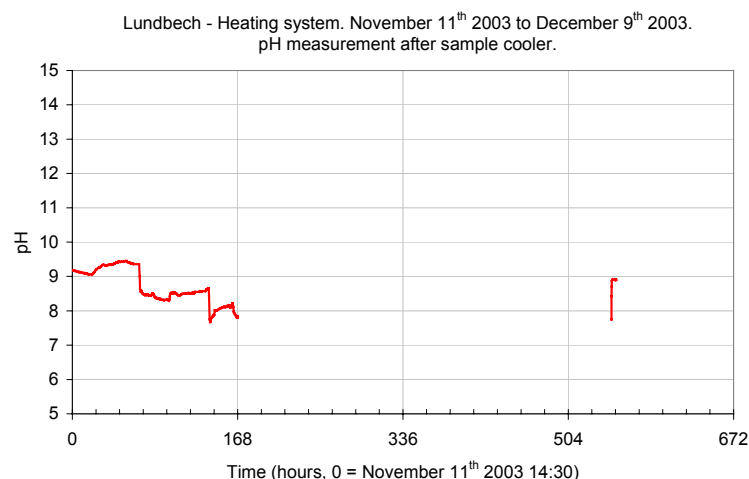


Figure 2. Circulating water pH-value measured in separate measuring panel after sample cooler.

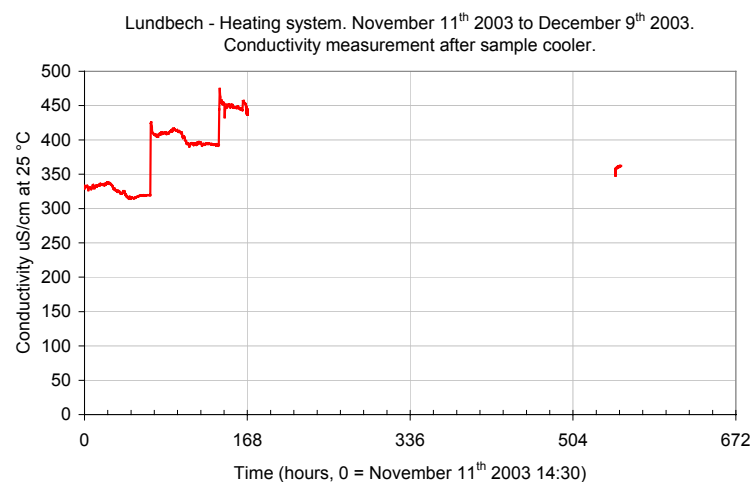


Figure 3. Circulating water conductivity measured in separate measuring panel after sample cooler.

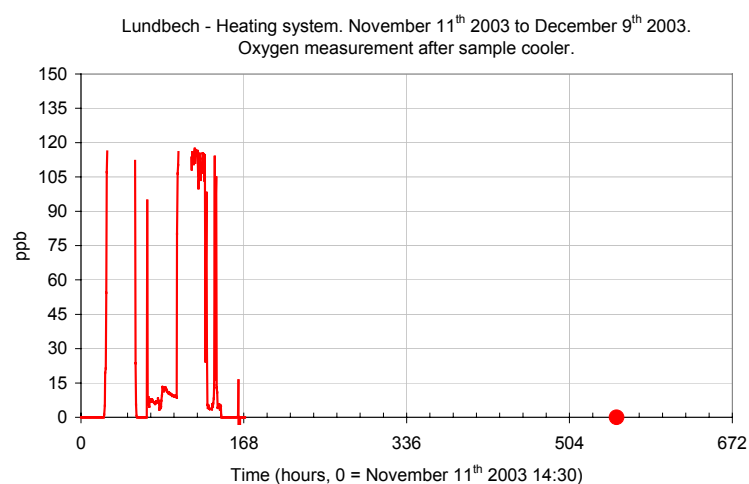


Figure 4. Circulating water oxygen content measured in separate measuring panel after sample cooler.

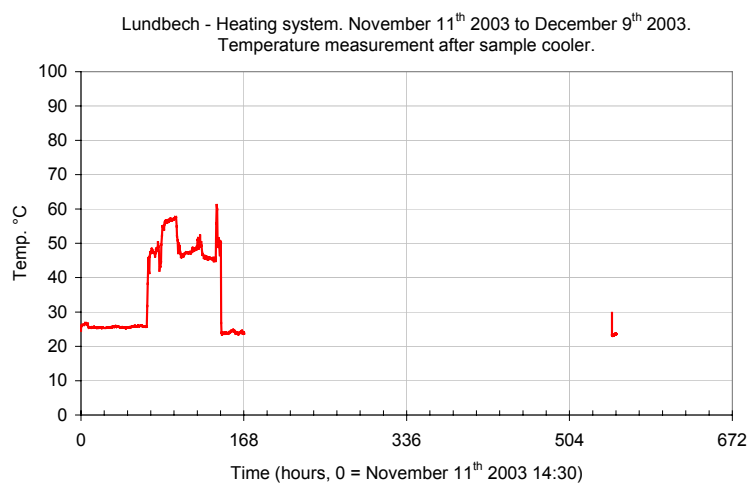


Figure 5. Temperature after sample cooler.

Appendix 2.

Corrosion measurements with ER-probes and LOCOR-CELL

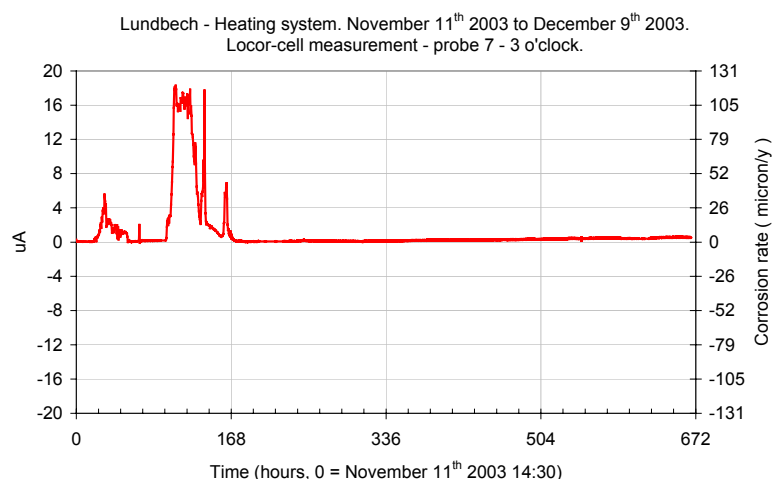


Figure 1. Measurements with the LOCOR-CELL. Probe 7 – 3 o'clock.
The measured corrosion rates shall be multiplied by a factor 5-10 to compensate for local corrosion attacks on the anode.

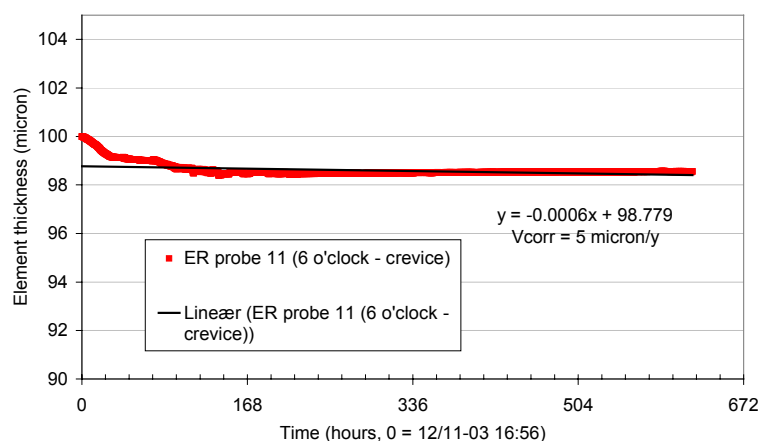


Figure 2. Measurements with covered ER-probe. Probe 11 – 6 o'clock.

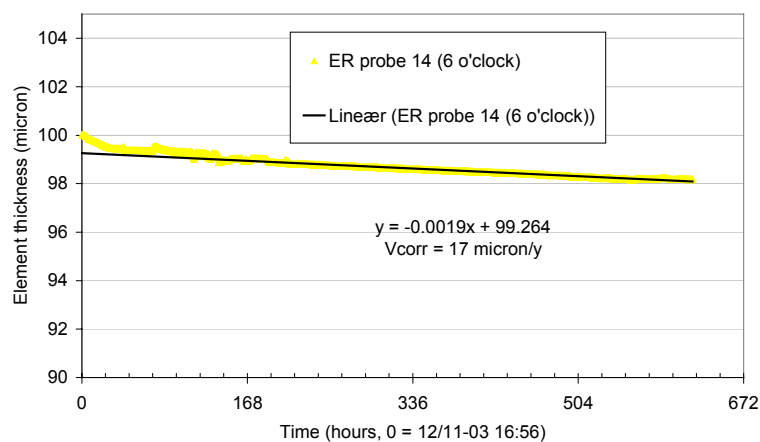


Figure 3. Measurements with ER-probe Probe 14 – 6 o'clock.

Appendix 3. Corrosion measures with three electrodes LPR and EIS

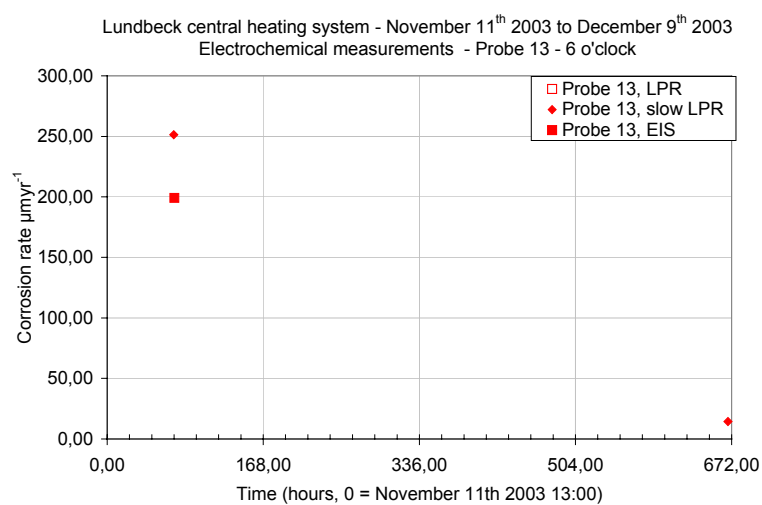


Figure 1. Probe 13 – 6 o'clock.

Weight loss coupons



Photo 1. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

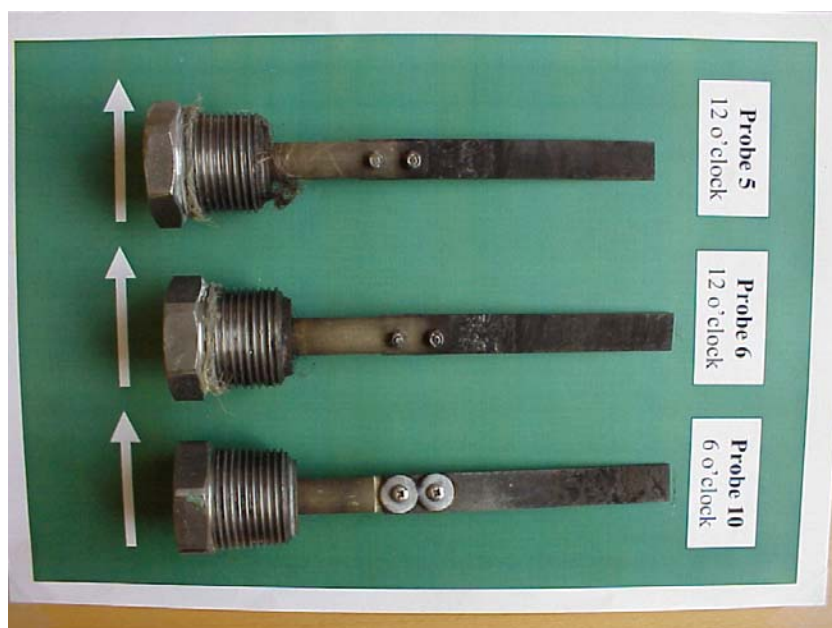


Photo 2. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

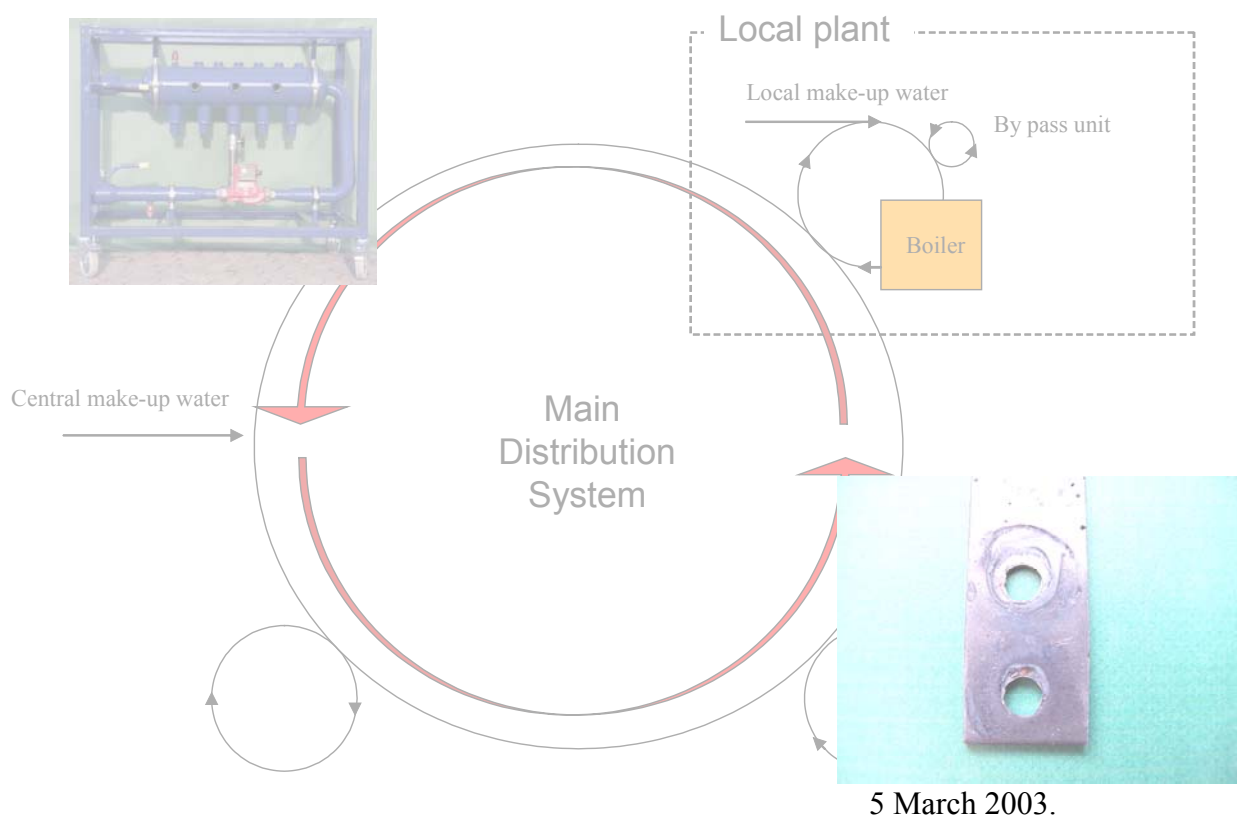
Measuring report from Odense distribution system – Næsbyhoved-Brody

**Monitoring of corrosion in district heating systems
(KORMOF)**

Joint Nordic project with support from Nordisk Industrifond (Nordic Innovation Centre)

Danish participants:
Force Technology (project management)
MetriCorr
Technical University of Denmark

Measurements sampled in the period from 13 December 2002 till 26 February 2004.



Summary and conclusions

In connection with the joint Nordic project *Corrosion monitoring in district heating systems* corrosion measurements in circulating water from Odense distributing system were sampled over the period from 13 December 2002 till 26 February 2004. The measurements were made on a by-pass unit mounted at the decentralised works at Næsbyhoved-Broby. Corrosion was determined on injected weight loss coupons, and through a limited period of time (13 January to 17 February 2003) the measuring program was intensified by performing concurrent environmental parameter measurements (pH, oxygen and conductivity) and measurements of the instantaneous corrosion rate at a number of contending on-line methods. The On-line methods' responses were compared to variations of the measured environmental parameters during a provoked decentralised addition of make-up water from the then cation exchange system. Furthermore, the on-line methods' reliability during usual operation was compared to results from the injected weight loss coupons. Unfortunately the circulation through the by-pass unit was interrupted during the period from April 2003 to February 2004 and the particular influence on the coupon weight loss is not known.

The overall result for all works is that highly sensitive ER (electric resistance) measurements is suitable for surveillance of general corrosion velocity and the LOCOR cell (crevice corrosion current) is suitable for surveillance of local corrosion risks. Both techniques have reacted fast to environmental changes in the systems and make possible continuous corrosion monitoring.

Highly sensitive ER may be interpreted as electronic weight loss measurements that on-line trace continuous variations in corrosion velocity over very short periods (hours). In comparison, credible weight loss measurements in such systems have required a measuring period of minimum 6 months.

Changes in crevice corrosion current measured with the LOCOR cell have clearly indicated presence of local corrosion but the final value of the current can only carefully be converted to corrosion velocity due to the localised character. The LOCOR cell gives response to changes in the risk of local corrosion within minutes and the results can thus be compared directly to changes in operation.

Two electrochemical methods – linearly polarisation measuring (LPM) and electrochemical impedance spectroscopy (EIS) – have been applied primarily for mechanism studies. The LPR method is used for commercial continuous corrossions surveillance/detection, but it is not recommendable in district heating systems, as it has resulted in a strong tendency to overrate the corrosion velocity. In general, the EIS method has resulted in more credible corrosion velocities but analysing the data is demanding and the measuring period is too long (several days) to register sudden changes.

As regards the on-going corrosion situation at the works is should be stressed and concluded that the make-up water then was very corrosive as corrosion velocities at as much as 1 mm/per year could be found. During normal operation it is indicated from the weight loss coupons that the corrosion velocity is less than 20 micrometer a year, probably close to zero, as the result from the weight loss coupons is based on corrosion accumulated both during normal operation and the feed water addition and the period with interrupted flow through the unit. As both the LOCOR cell and the ER measurements during normal operation showed very low corrosion velocities ($<2 \mu\text{m}/\text{year}$) it seems reasonable that the general corrosion velocity during normal operation is close to zero.

Background

System: The system is a distribution system with approximately 2x2200 km current network and approximately 80.000 users. Approximately 95% of the heat is supplied from Fynsværket. The remaining 5% is supplied from a total of 20 heating centrals. Most centrals are operating only at peak loads. The operating pressure is at 3 – 6 bar.

Make-up water: The make-up water consumption is now approximately 700 – 800 m³/day (as was informed at initiating visits to the site on 28-09-2001). Make-up water is supplied and dosed centrally from the Fynsværket as vacuum deaerated RO-water. A small part of the make-up water (approx. 3%) is supplied decentrally from heating centrals. All heating centrals have been equipped with their own system for water treatment, usually cation exchangers. On-going decentralised experiments are being made with micro bubble aeration, however, only for small amounts of make-up water. In practice the experience is that micro-bubble systems lower the oxygen content to 1,5 ppm at 80°C.

Circulating water: The oxygen content is stated as low (less than 20 ppb) and the conductivity between 40 and 80 µS/cm. There is no use of oxygen binding agents or other additives. The pH-value is regulated based at the Fynsværket with sodium hydroxide. The pH-value has previously been regulated decentrally, but practical experience has shown that correct dosage in decentralised works is difficult.

Experience with corrosion and damages to the supply network. No experience with corrosion inside the pipes. However, deposits of reddish corrosion products have been found in the return stream (after make-up water addition) at the Næsbyhoved Broby heating central.

Test program

Location of bypass-unit: The bypass unit is mounted at Næsbyhoved Broby heating central at return stream after make-up water addition. At the measuring time, the make-up water at Næsbyhoved Broby heating central was treated with a cation exchanger. The cation exchanger has subsequently been replaced by other make-up water treatment.

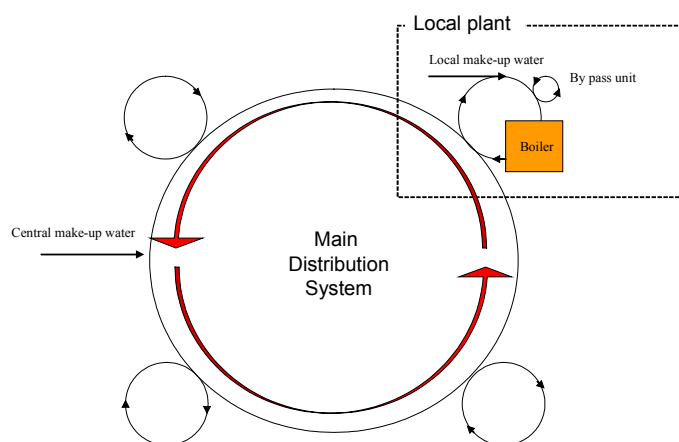


Figure 1a. Schematic presentation of the bypass-unit's location. Pipeline network at Odense.



Figure 1b. Photo of bypass-unit with circulation pump before probe mountings.

Corrosion measurements have been made with 5 methods, to which has been applied a total of 4 different probe types: Weight loss coupons, ER-probes, LOCOR-CELL and three electrodes for LPR and EIS measurements. Measurements have been performed in the bypass units measuring chamber, where it is possible to mount probes, both at the bottom, the side and the top. Probes mounted at the bottom of the measuring chamber are partly sheltered from the water flow, see Figure 2.

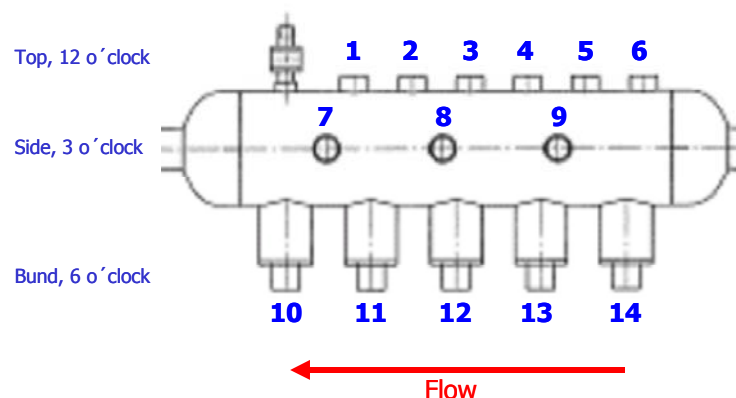


Figure 2. Probe locations in bypass-unit.

- 1: Weight loss coupon including steel disc for biofilm analysis
- 2: Empty
- 3: Three- electrode.
- 4: ER-probe
- 5: Weight loss coupon including steel disc for biofilm analysis
- 6: Weight loss coupon including steel disc for biofilm analysis
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- 8: Thermo sensor
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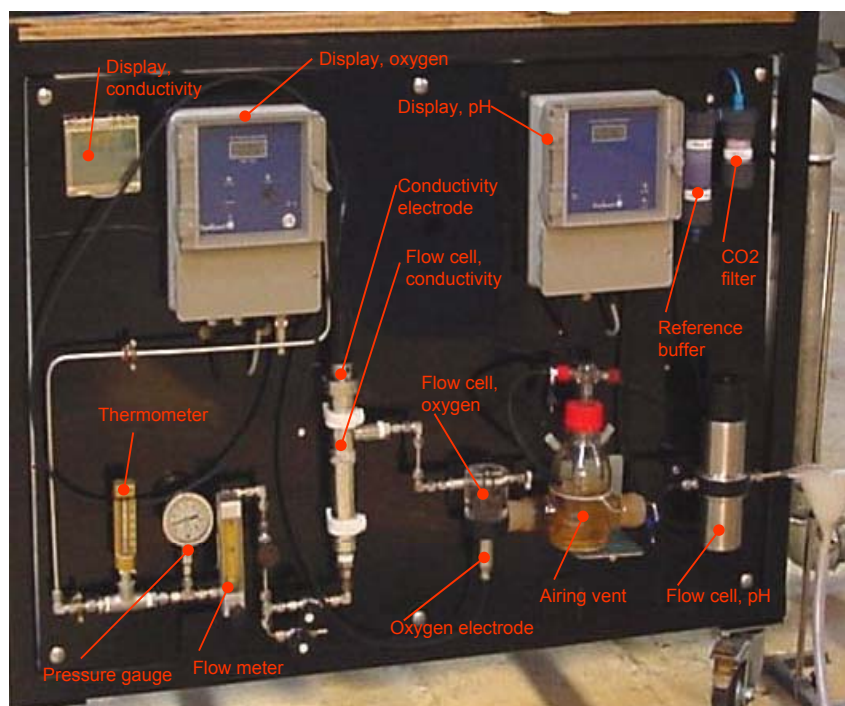


Figure 3. Photo of separate measuring panel for measuring water parameters.

All measurements (weight loss coupons excepted) are gathered on-line in a data logger. The Measurements can be traced centrally and at sight they may be included in the works' usual electronic surveillance.

Measuring results

Measuring results have been reproduced schematically below and are shown in curves in appendices 1-4.

For the first part of the measuring period when the environment is stable, the corrosion rate is acceptably low and the environment is satisfactory. Through the heavy make-up water dosage significant changes occur both in the environment and in the corrosion rate. Both ER and the LOCOR cell give heavy responses, which indicate very high corrosion rates. LPR measurements heavily over estimate the corrosion rate at the first part of the test and the curves are not linear indicating that the method should not be used. The electrochemical measurements indicate higher rates at the bottom of the unit than at the top of it. Measuring with commercial electrochemical equipment gives rates within the range of the traditional LPR and significant increase in corrosion is seen during make-up water addition. The pitting index is a measure for the inclination to pitting and a definite increase is observed at the addition of make-up water as a sign that the risk for crevice corrosion has increased. The system is exposed to a short period of heavy corrosion caused by poorly treated make-up water, and the make-up water dosage had such extend that only make-up water circulated in the unit. We highly recommend that better make-up water quality be applied otherwise severe dilution will take place.

Table 1. Schematic overview of measuring results.

Parameter	Measuring period	Normal operation	Event no. 2	Event no. 3
	Day + night no.	0-22	1	20
Temperature, °C	0-22	42	39	10
Conductivity $\mu\text{S}/\text{cm}$	0-22	70	70	800
PH	0-22	9,95	9,9	7,6
Oxygen, ppb	0-22	0-1	110	~500 (600)
ER, $\mu\text{m}/\text{year}$, probe 4, top	-	-	-	-
ER, $\mu\text{m}/\text{year}$, probe 11, bottom		0	-	430-870
LOCOR-Cell, Probe 7 – 3 o'clock.	0-22	2	??	33-400
LPR, $\mu\text{m}/\text{year}$, probe 3, top	10	52	-	-
LPR, $\mu\text{m}/\text{year}$, probe 13, bund	18	108	-	-
EIS, $\mu\text{m}/\text{year}$, probe 3, top	10	9,3	-	-
EIS, $\mu\text{m}/\text{year}$, probe 13, bund	-	-	-	-
Weight loss, probe 5, top	0-440	10	-	-
Weight loss, probe 6, top	0-440	15	-	-
Weight loss, probe 10, bottom	0-440	19	-	-
IC LPR, $\mu\text{m}/\text{year}$, probe 3, top	0-10	60		225
IC LPR, $\mu\text{m}/\text{year}$, probe 13, bottom	10-18	250-100		
Pitting index, probe 3, top	0-10	<0,01		1 – 0,02
Pitting index, probe 13, bottom	10-18	0,006-0,03		

Table 2. Events over the test period.

Event no.	Description
0	Unit mounted 13-12-2002
1	Measurements started on 14-01-2003 at 13:00 and ended on 19-02-2003 at 10:30
2	Testing of heaters/boilers. After 20 hours.
3	Make-up water dosage. Start on 10-02-2003 at 14:00; ended on 11-02-2003 at 11:00
4	Measurements ended

Appendix 1. Measurements of water parameters

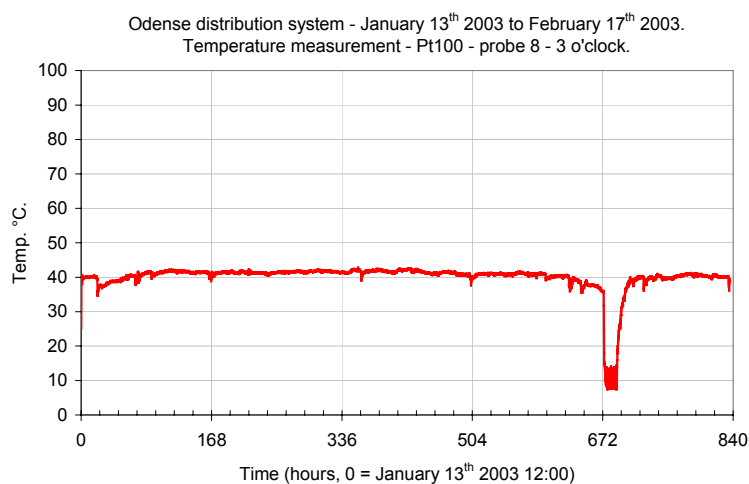


Figure 1. Circulating water temperature measured in the bypass unit. Probe 8 – 3 o'clock.

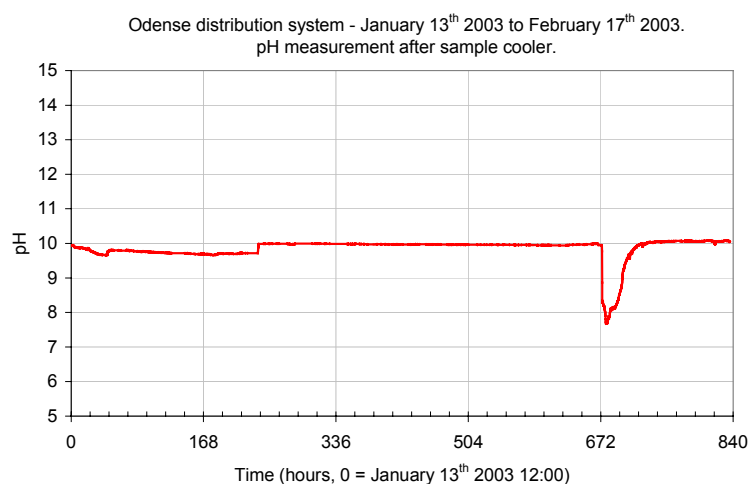


Figure 2. Circulating water pH-value measured in separate measuring panel after sample cooler.

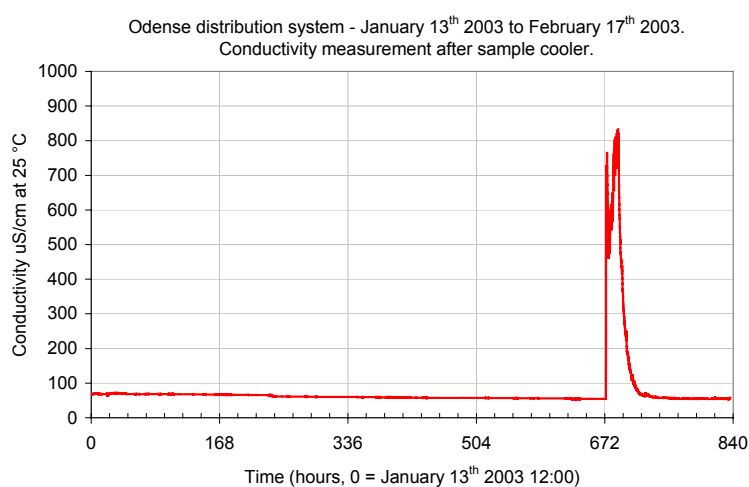


Figure 3. Circulating water conductivity measured in separate measuring panel after sample cooler.

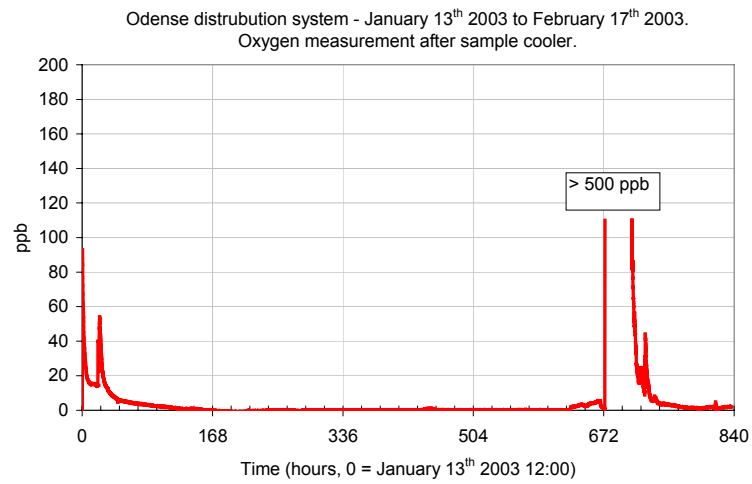


Figure 4. Circulating water oxygen content measured in separate measuring panel after sample cooler.

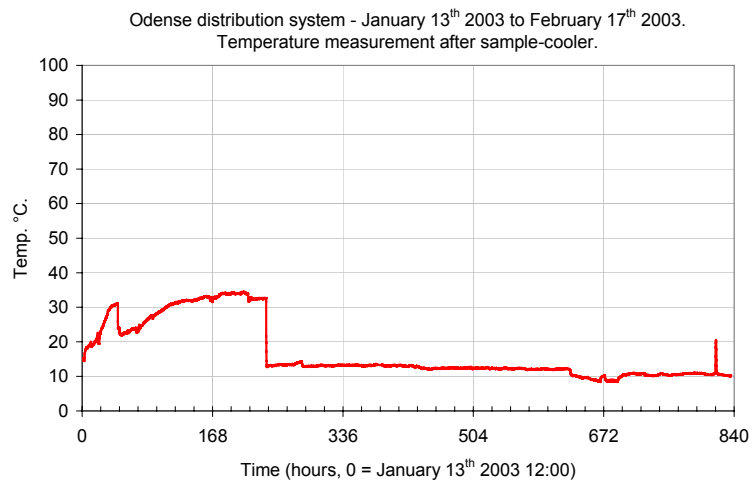


Figure 5. Temperature after sample cooler.

Appendix 2.

Corrosion measurements with ER-probes and LOCOR-CELL

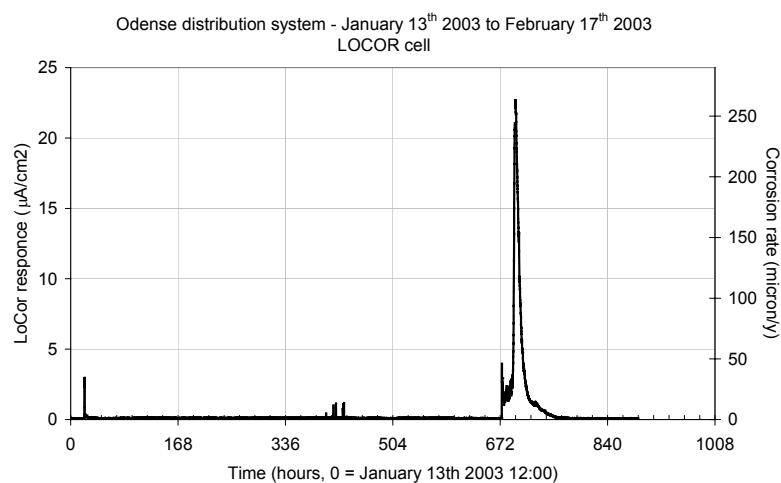


Figure 1. Measurements with the LOCOR-CELL. Probe 7 – 3 o'clock.
The measured corrosion rates shall be multiplied by a factor 5-10 to compensate for local corrosion attacks on the anode.

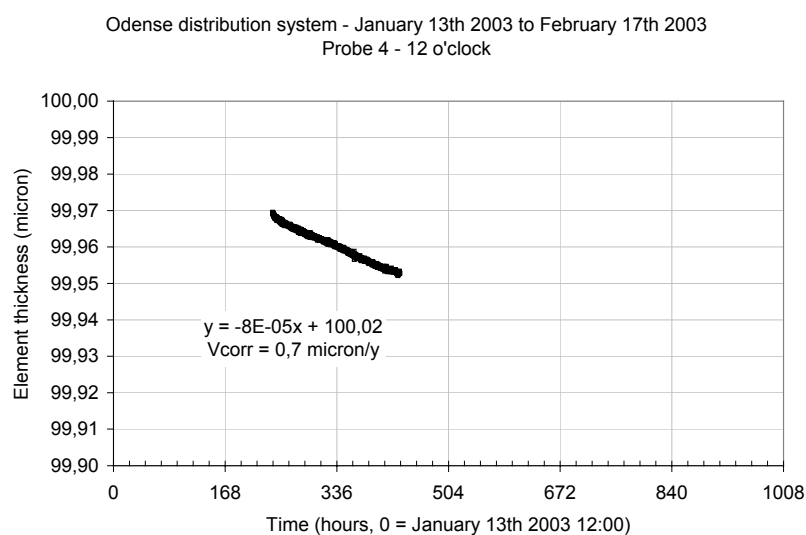


Figure 2. Measurements with ER-probe. Probe 4 – 12 o'clock.

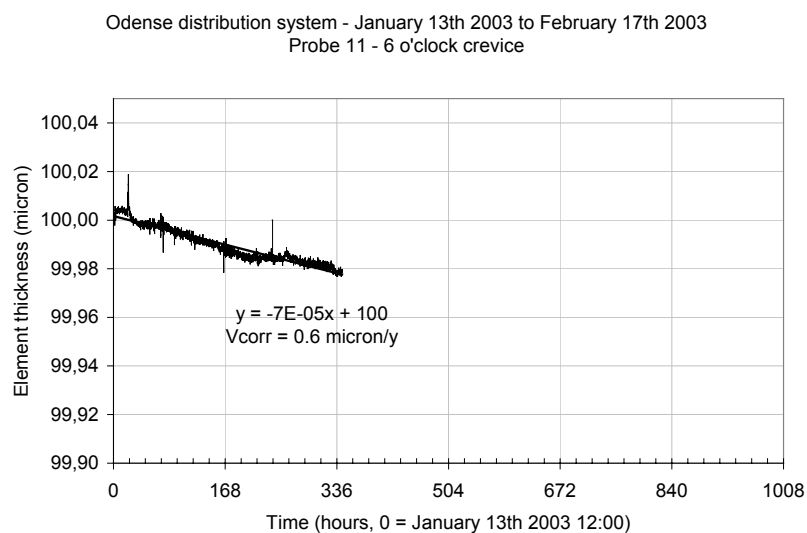


Figure 3. Measurements with covered ER-probe. Probe 11 – 6 o'clock.

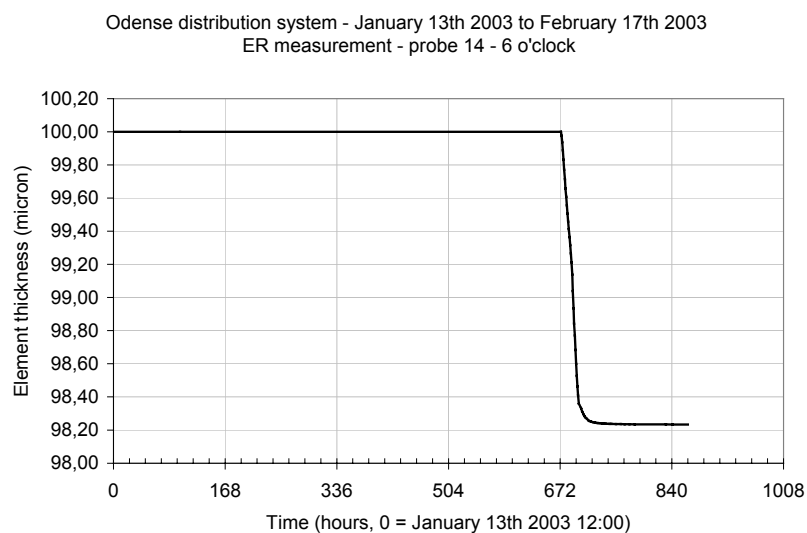


Figure 4. Measures with ER-probe. Probe 14 – 6 o'clock.

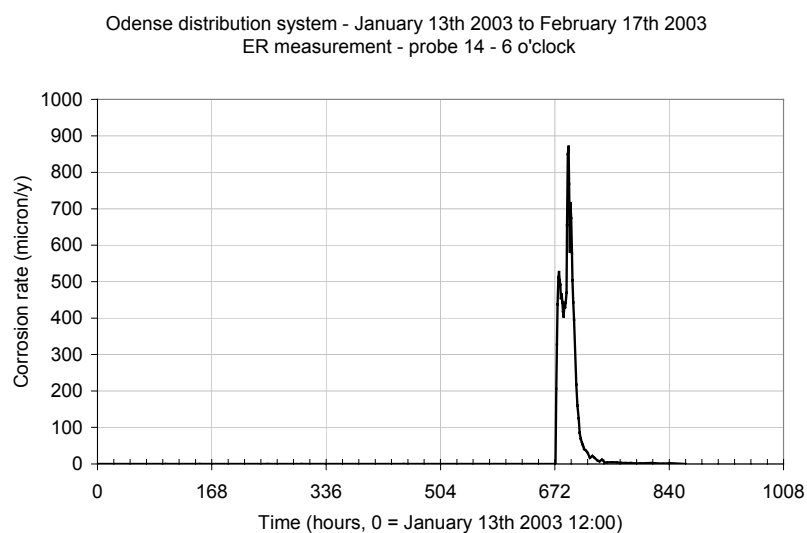


Figure 5. Measurements with ER-probe Probe 14 – 6 o'clock.

Appendix 3.

Corrosion measures with three electrodes LPR and EIS

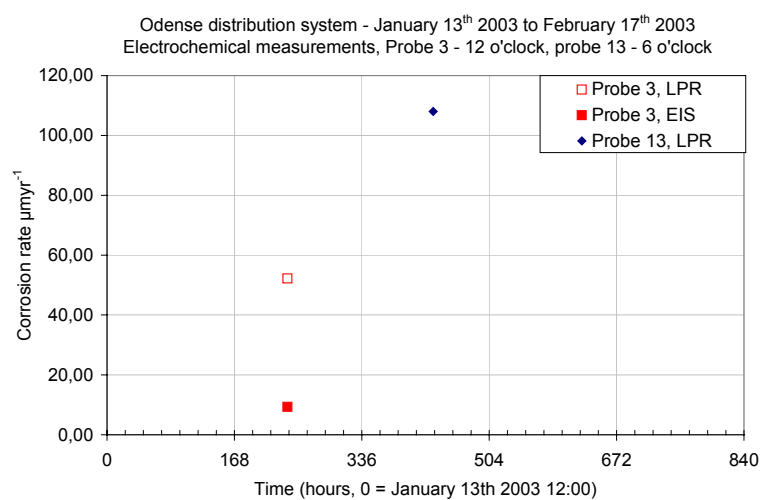


Figure 1. Probe 3 – 12 o'clock and Probe 13 – 6 o'clock.

Corrosion measurements with InterCorr equipment

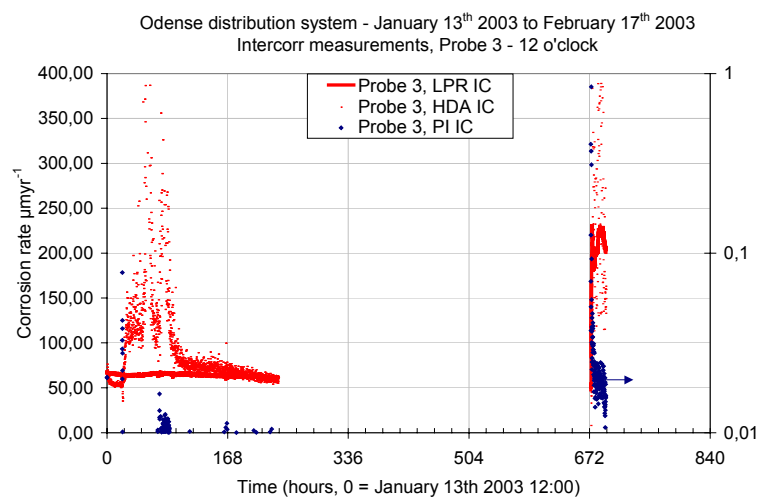


Figure 1. Probe 3 – 12 o'clock.

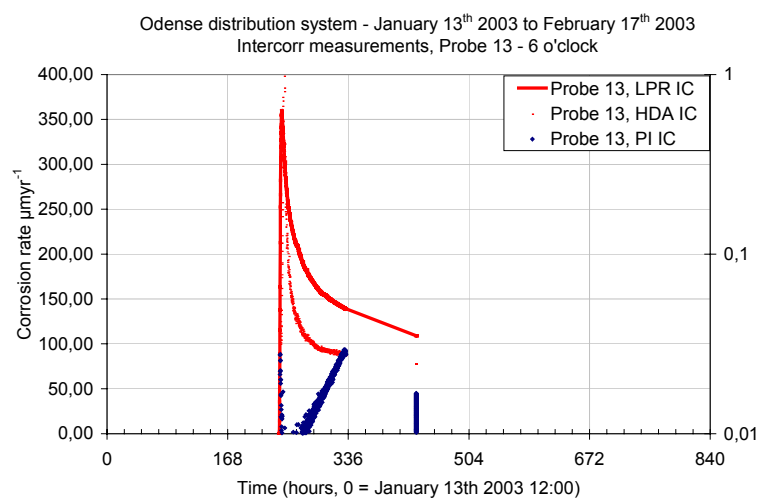


Figure 2. Probe 13 – 6 o'clock.



Photo 1. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.



Photo 2. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

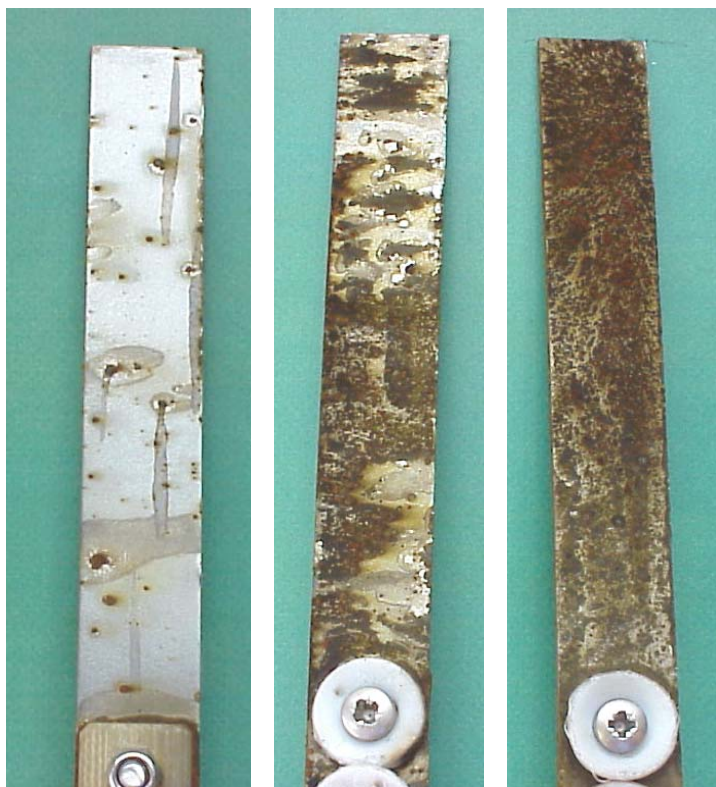


Photo 3. Weight loss coupons in detail. Seen from the left probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

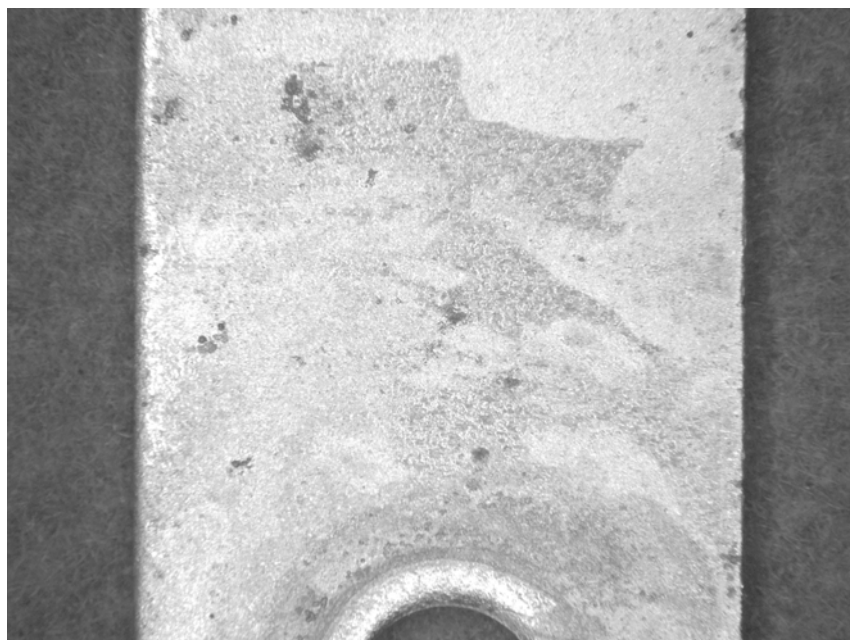


Photo 4. Weight loss coupon in detail probe 6 - 12 o'clock after cleansing. Approximately 6x enlargement.

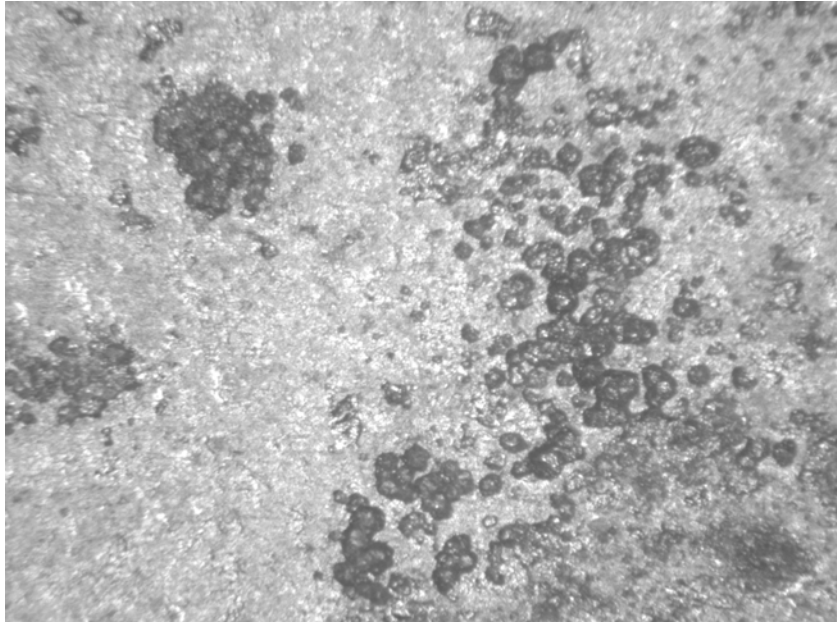


Photo 5. Weight loss coupon in detail probe 6 - 12 o'clock after cleansing. Approximately 50x enlargement.

Measuring report from VEKS distribution system – Karlslunde

Monitoring of corrosion in district heating systems (KORMOF)

Joint Nordic project with support from Nordisk Industrifond (Nordic Innovation Centre)

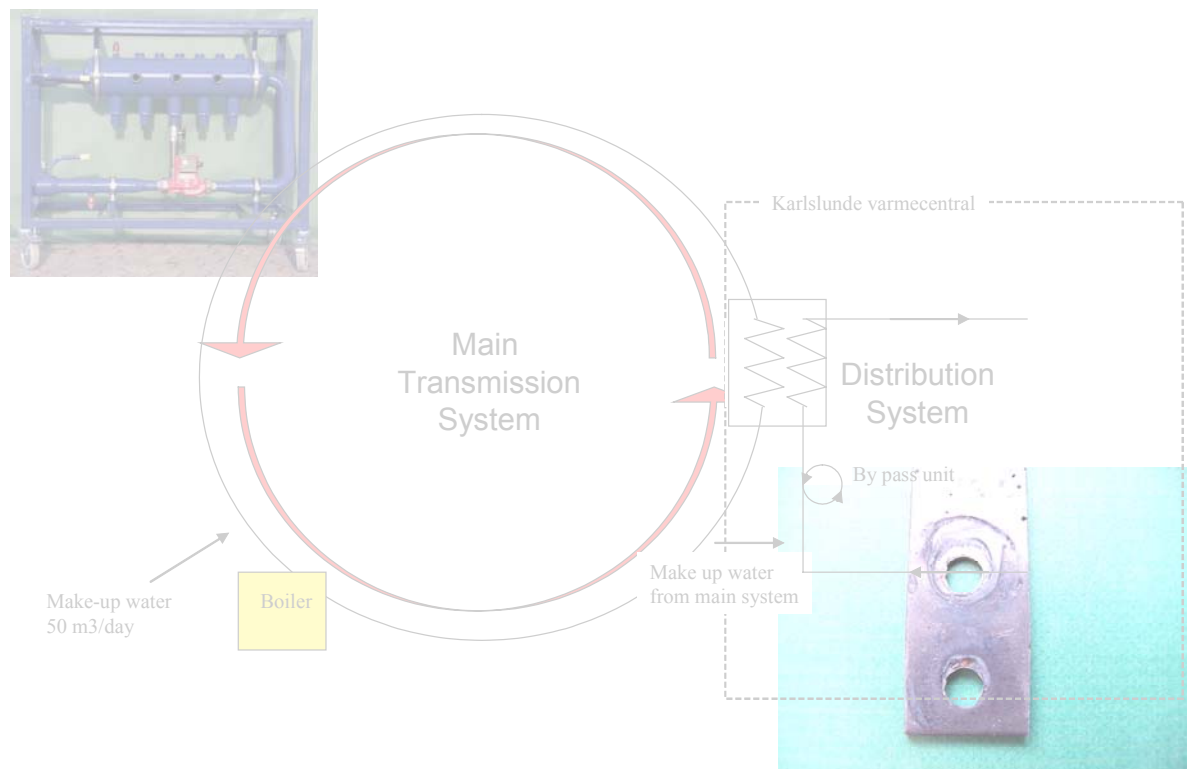
Danish participants:

Force Technology (project management)

MetriCorr

Technical University of Denmark

Measurements sampled in the period from 13 February 2003 till 18 February 2004.



Summary and conclusions

In connection with the joint Nordic project *Corrosion monitoring in district heating systems* corrosion measurements in circulating water from VEKS distribution system were sampled over the period from 13 February 2003 till 18 February 2004. The measurements were made on a by-pass unit mounted at the decentralised works at Karlslunde. Corrosion was determined on injected weight loss coupons, and through a limited period of time (28 February to 27 March 2003) the measuring program was intensified by performing concurrent environmental parameter measurements (pH, oxygen and conductivity) and measurements of the instantaneous corrosion rate at a number of contending on-line methods. The On-line methods' responses were compared to variations of the measured environmental parameters. Furthermore, the on-line methods' reliability during usual operation was compared to results from the injected weight loss coupons. Unfortunately the by-pass unit was interrupted in a few hours immediately after the intensified period of measurements and the particular influence on the coupon weight loss is not known.

The overall result for all works is that highly sensitive ER (electric resistance) measurements is suitable for surveillance of general corrosion velocity and the LOCOR cell (crevice corrosion current) is suitable for surveillance of local corrosion risks. Both techniques have reacted fast to environmental changes in the systems and make possible continuous corrosion monitoring.

Highly sensitive ER may be interpreted as electronic weight loss measurements that on-line trace continuous variations in corrosion velocity over very short periods (hours). In comparison, credible weight loss measurements in such systems have required a measuring period of minimum 6 months.

Changes in crevice corrosion current measured with the LOCOR cell have clearly indicated presence of local corrosion but the final value of the current can only carefully be converted to corrosion velocity due to the localised character. The LOCOR cell gives response to changes in the risk of local corrosion within minutes and the results can thus be compared directly to changes in operation.

Two electrochemical methods – linearly polarisation measuring (LPM) and electrochemical impedance spectroscopy (EIS) – have been applied primarily for mechanism studies. The LPR method is used for commercial continuous corrosion surveillance/detection, but it is not recommendable in district heating systems, as it has resulted in a strong tendency to overrate the corrosion velocity. In general, the EIS method has resulted in more credible corrosion velocities but analysing the data is demanding and the measuring period is too long (several days) to register sudden changes.

As regards the on-going corrosion situation at the works it should be stressed and concluded that the environment was very stable during the intensified period of measurements. During normal operation it is indicated from the weight loss coupons that the average corrosion rate is less app. 8 micrometers a year, which is relatively high compared with measurements from ER probes and the LOCOR cell. Corrosion attacks observed on the weight loss coupons are uniform and no pits were observed. As both the LOCOR cell and the ER measurements during normal operation showed very low corrosion rates ($<2 \mu\text{m}/\text{year}$) it seems reasonable that the general corrosion rate during normal operation is close to zero. The difference in corrosion rates on the weight loss coupons and on the ER probes and the LOCOR cell might very well be explained by the few hours' interruption of the by-pass unit. The difference could also be explained by changes in the environment apart from the intensified period of measurements.

Background

System: The system is a distribution system where the heat is supplied from VEKS' transmission system and in some extends from smaller heating plants. The operating pressure is less than 6 bars at the return stream.

Make-up water: Make-up water is supplied directly from VEKS' transmission system.

Circulating water: The oxygen content is stated as low (less than 20 ppb) and the conductivity between 80 and 90 $\mu\text{S}/\text{cm}$. The pH-value is stated as 9,8-10,0.

Experience with corrosion and damages to the supply network. No experience with corrosion inside the pipes.

Test program

Location of bypass-unit: The bypass unit is mounted at Karlslunde heating central at return stream after make-up water addition. At the measuring time, the make-up water was supplied from VEKS' transmission system.

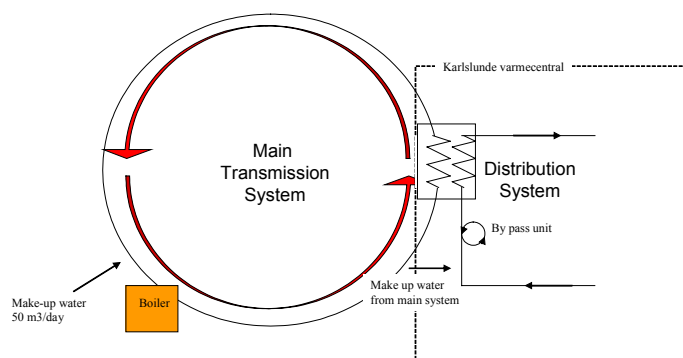


Figure 1a. Schematic presentation of the bypass-unit's location.



Figure 1b. Photo of bypass-unit with circulation pump before probe mountings.

Corrosion measurements have been made with 5 methods, to which has been applied a total of 4 different probe types: Weight loss coupons, ER-probes, LOCOR-CELL and three electrodes for LPR and EIS measurements. Measurements have been performed in the by-pass units measuring chamber, where it is possible to mount probes, both at the bottom, the side and the top. Probes mounted at the bottom of the measuring chamber are partly sheltered from the water flow, see Figure 2.

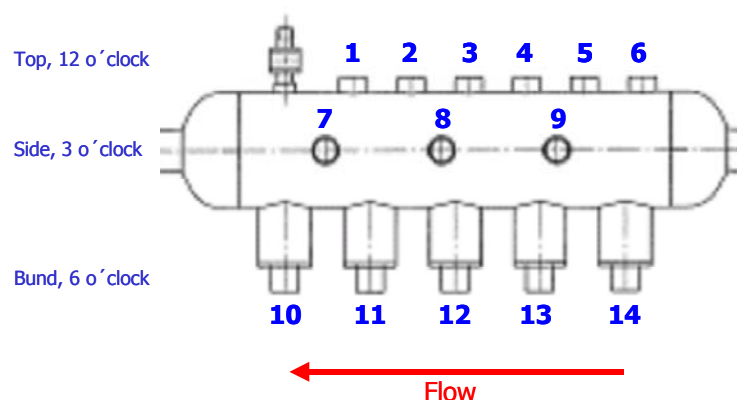


Figure 2. Probe locations in bypass-unit.

- 1: Weight loss coupon including steel disc for biofilm analysis
- 2: Empty
- 3: Three- electrode.
- 4: ER-probe
- 5: Weight loss coupon including steel disc for biofilm analysis
- 6: Weight loss coupon including steel disc for biofilm analysis
- 7: LOCOR-CELL
- 8: Thermo sensor
- 9: Empty
- 10: Weight loss coupon including steel disc for biofilm analysis
- 11: ER-probe with simulated deposits/crevice
- 12: Weight loss coupon including steel disc for biofilm analysis mounted in an extended bottom branch piece for simulation of a dead end
- 13: Three electrode
- 14: ER-probe.

Online measuring of water parameters (pH, conductivity and oxygen content) has been measured in a separate measuring panel, Figure 3, on an individual stream taken from the bypass-unit. Prior to measuring water parameters the individual stream is cooled in a sample cooler.

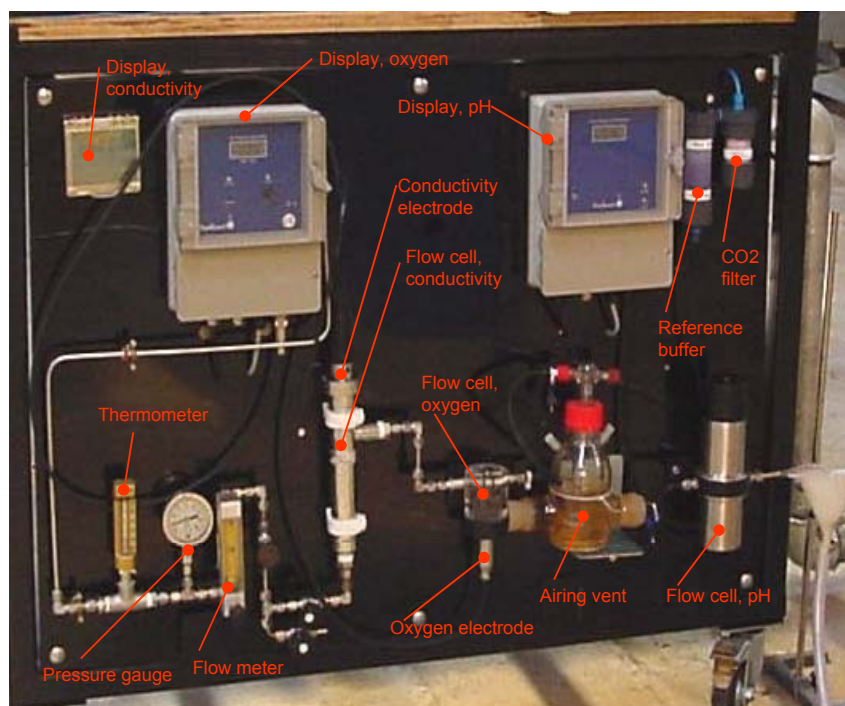


Figure 3. Photo of separate measuring panel for measuring water parameters.

All measurements (weight loss coupons excepted) are gathered on-line in a data logger. The Measurements can be traced centrally and at sight they may be included in the works' usual electronic surveillance.

Measuring results

Measuring results have been reproduced schematically below and are shown in curves in appendices 1-3. Photos of weight loss coupons are shown in appendix 4.

During the intensified measuring period the environment was stable, the corrosion rate is acceptably low although pH is relatively low compared with the Danish recommendations. In this environment with high pH, low oxygen and low conductivity corrosion should be negligible. This is confirmed from the ER-probes and the LOCOR cell. LPR and EIS measurements heavily over estimate the corrosion rate. The system must be considered stable with low corrosion rates although effects of changes in the environment cannot be assessed due to the stable environment during measurements

Table 1. Schematic overview of measuring results.

Parameter	Measuring period	Normal operation
	Day + night no.	0-22
Temperature, °C	0-28	35-55 ¹
Conductivity $\mu\text{S}/\text{cm}$	0-28	80-90
PH	0-28	9,2-9,4
Oxygen, ppb	0-28	0-0,6
ER, $\mu\text{m}/\text{year}$, probe 4, top	-	-
ER, $\mu\text{m}/\text{year}$, probe 11, bottom	7-28	1-2
ER, $\mu\text{m}/\text{år}$, probe 14, bottom	7-28	1
LOCOR-Cell, Probe 7 – 3 o'clock.	0-28	1
LPR, $\mu\text{m}/\text{year}$, probe 3, top	0/20	26/15
LPR, $\mu\text{m}/\text{year}$, probe 13, bund	0/15	36/30
EIS, $\mu\text{m}/\text{year}$, probe 3, top	3/20	31/20
EIS, $\mu\text{m}/\text{year}$, probe 13, bund	0/15	47/34
Weight loss, probe 5, top	370	9
Weight loss, probe 6, top	370	8
Weight loss, probe 10, bottom	370	8

1: Temperature varies during 24 hours due to heaters/boilers starting in the morning for extra capacity.

Table 2. Events over the test period.

Event no.	Description
0	Unit mounted 13-02-2003
1	Online measurements started on 28-02-2003
2	Testing of equipment for measuring pH, conductivity and oxygen, 26-03-2003
3	Online measurements ended on 27-03-2003
4	Measurements ended 18-02-2004

Appendix 1. Measurements of water parameters

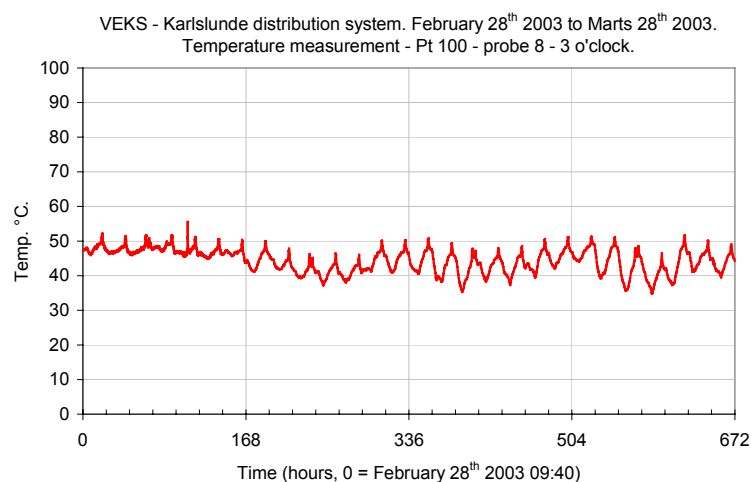


Figure 1. Circulating water temperature measured in the bypass unit. Probe 8 – 3 o'clock.

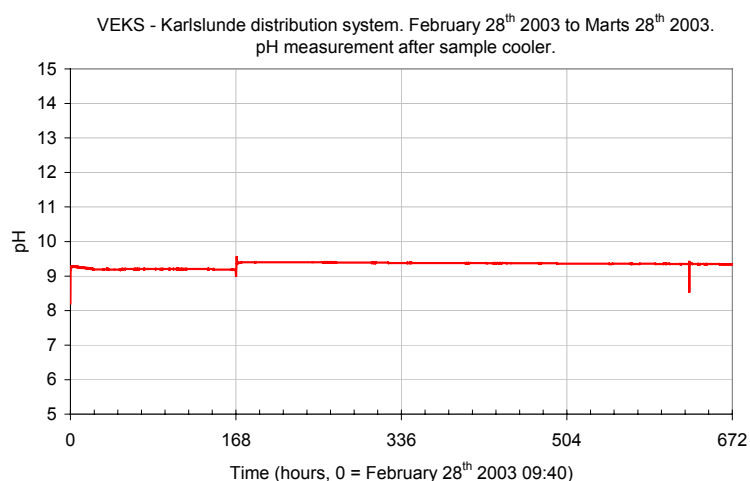


Figure 2. Circulating water pH-value measured in separate measuring panel after sample cooler. The drop in pH after 671 days and nights (26-03-2003) is caused due to test of the equipment for measuring pH, conductivity and oxygen.

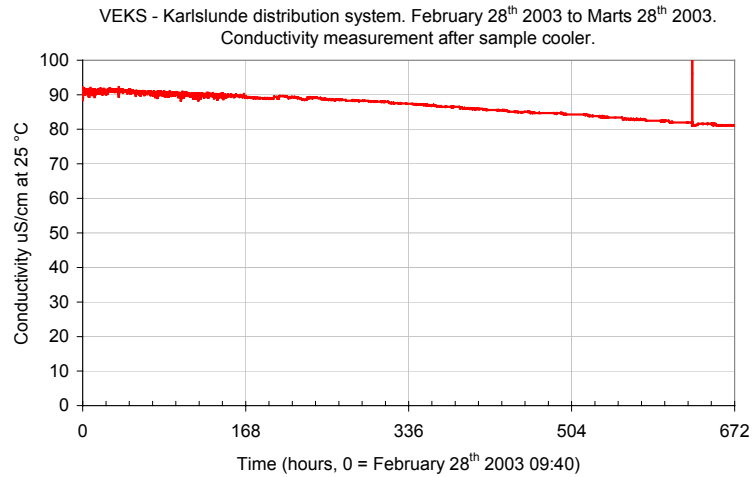


Figure 3. Circulating water conductivity measured in separate measuring panel after sample cooler. The rise in conductivity after 671 days and nights (26-03-2003) is caused due to test of the equipment for measuring pH, conductivity and oxygen.

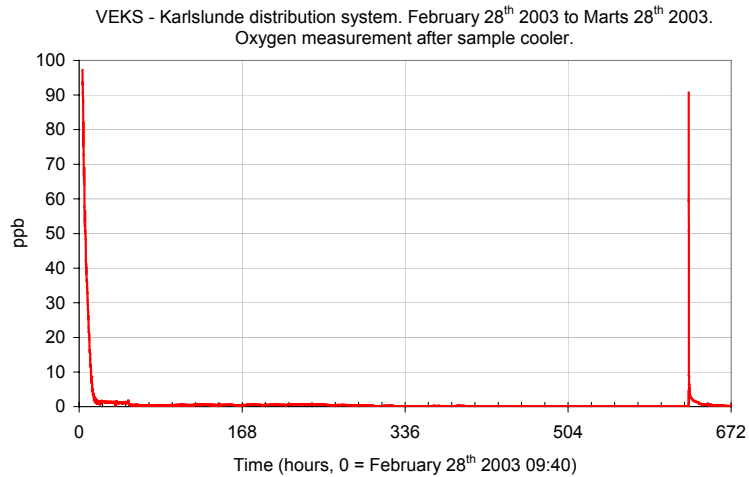


Figure 4. Circulating water oxygen content measured in separate measuring panel after sample cooler. The rise in oxygen after 671 days and nights (26-03-2003) is caused due to test of the equipment for measuring pH, conductivity and oxygen.

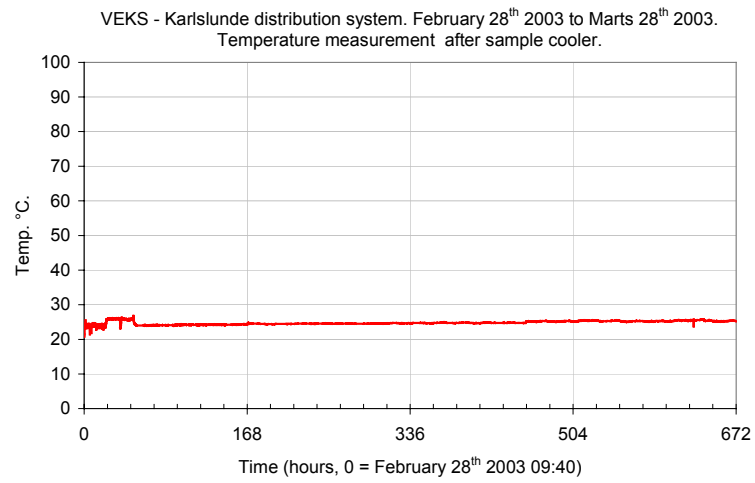


Figure 5. Temperature after sample cooler.

Appendix 2.

Corrosion measurements with ER-probes and LOCOR-CELL

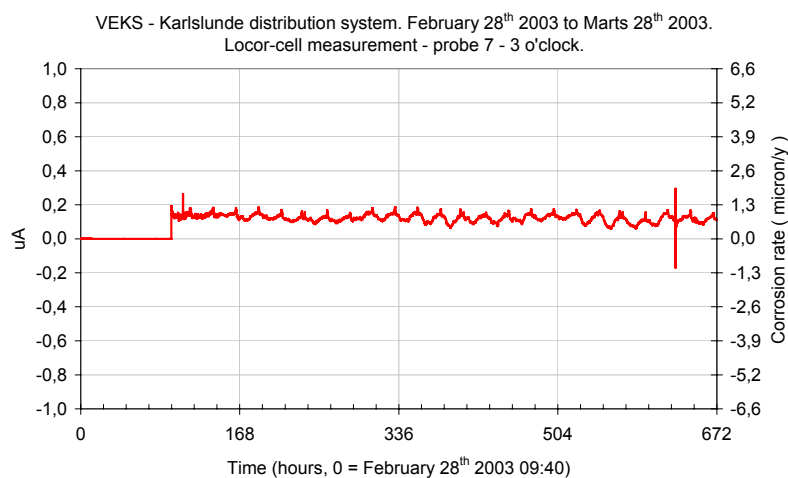


Figure 1. Measurements with the LOCOR-CELL. Probe 7 – 3 o'clock.
The measured corrosion rates shall be multiplied by a factor 5-10 to compensate for local corrosion attacks on the anode.

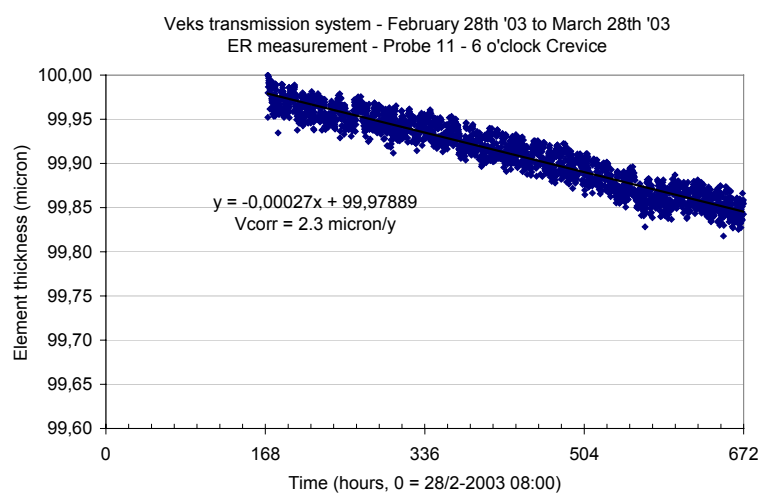


Figure 2. Measurements with covered ER-probe. Probe 11 – 6 o'clock.

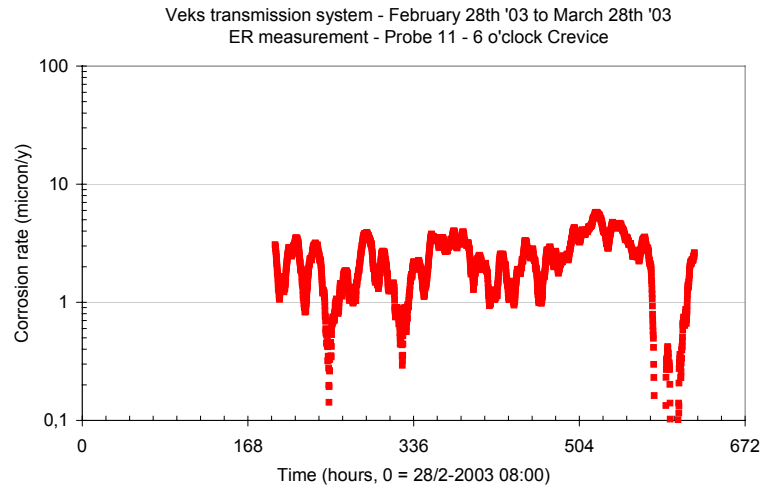


Figure 3. Measurements with covered ER-probe. Probe 11 – 6 o'clock.

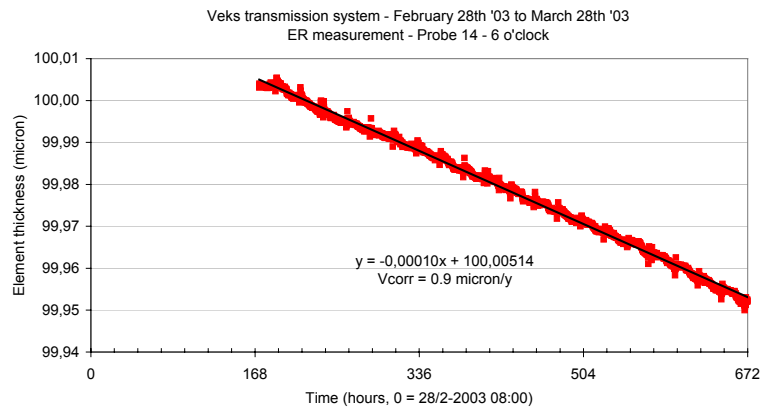


Figure 4. Measures with ER-probe. Probe 14 – 6 o'clock.

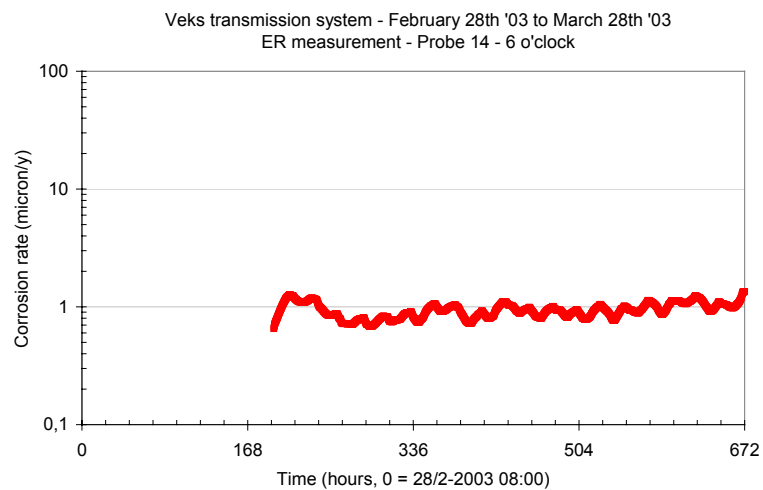


Figure 5. Measurements with ER-probe Probe 14 – 6 o'clock.

Appendix 3. Corrosion measures with three electrodes LPR and EIS

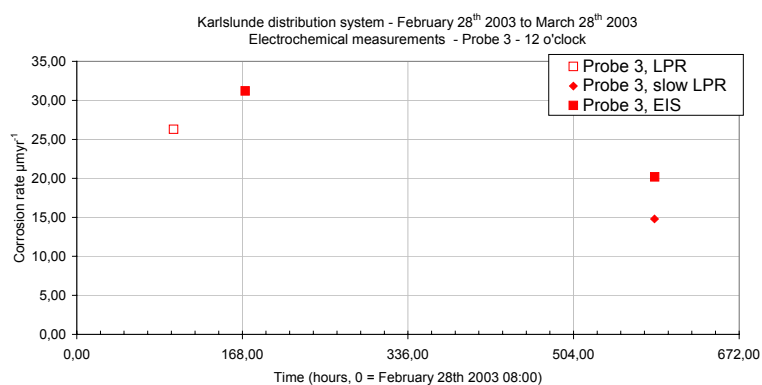


Figure 1. Probe 3 – 12 o'clock.

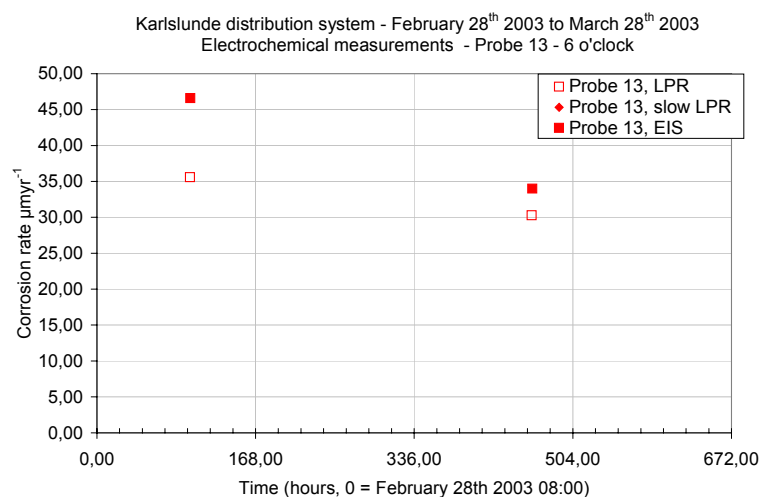


Figure 2. Probe 13 – 6 o'clock.



Photo 1. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.



Photo 2. Overview of weight loss coupons probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

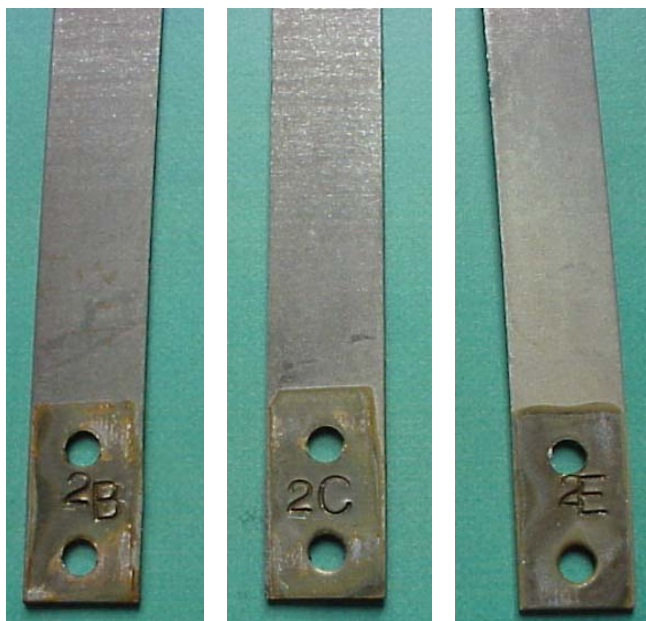


Photo 3. Weight loss coupons in detail. Seen from the left probe 5 - 12 o'clock, probe 6 - 12 o'clock and probe 10 - 6 o'clock.

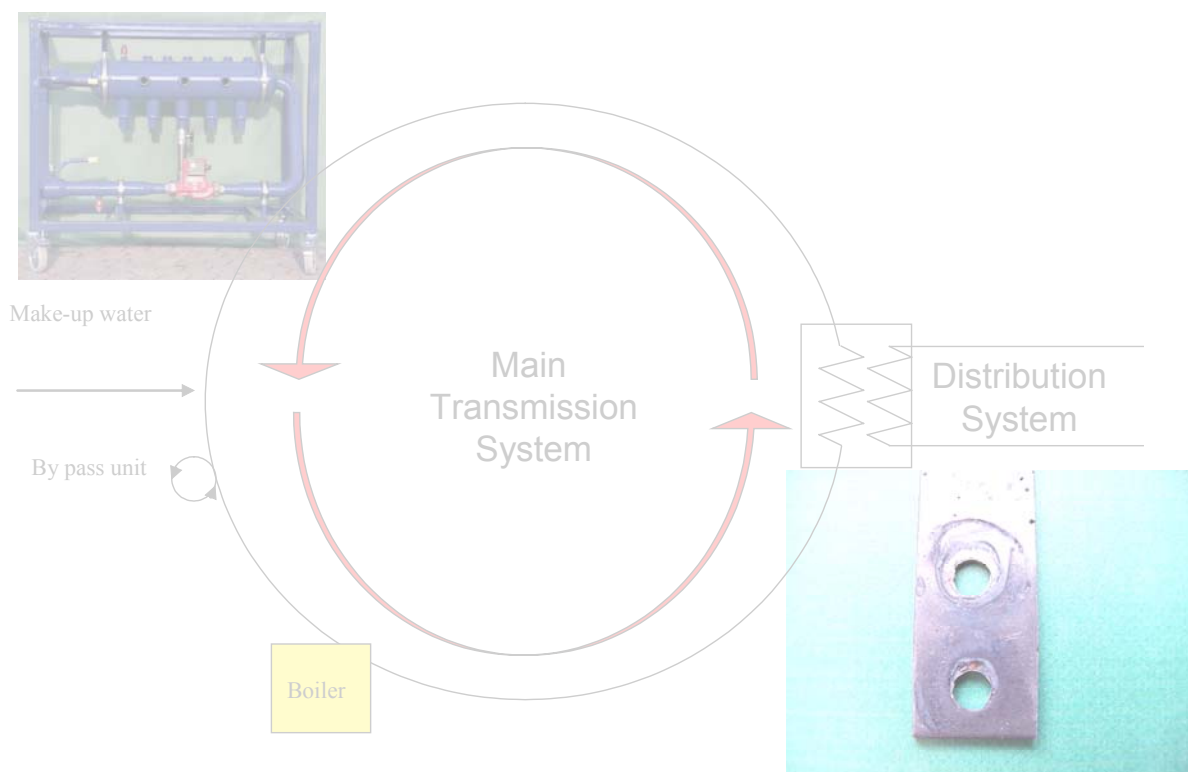
Measuring report from Viborg distribution system

Monitoring of corrosion in district heating systems (KORMOF)

Joint Nordic Projects with support from Nordisk Industrifond (Nordic Innovation Centre)

Danish participants:
Force Technology (project management)
MetriCorr
Technical University of Denmark

Measurements sampled in the period from 19. June 2003 to 1 March 2004.



Summary and conclusions

In connection with the joint Nordic project *Corrosion monitoring in district heating systems* corrosion measurements in circulating water from Viborg distributing system were sampled over the period from 19 June 2003 till 1 March 2004

The measurements were made on a by-pass unit mounted at the decentralised works at Viborg distribution system. Corrosion was determined on injected weight loss coupons, and over a limited period of time (6 August to 1 September 2003) the measuring program was intensified by performing concurrent environmental parameter measurements (pH, oxygen and conductivity) and measurements of the instantaneous corrosion rate at a number of contending on-line methods. The On-line methods' responses were compared to variations of the measured environmental parameters during a provoked decentralised addition of make-up water from the then cation exchange system. Furthermore, the on-line methods' reliability during usual operation was compared to results from the injected weight loss coupons. Unfortunately the circulation through the by-pass unit was interrupted during the period from September 2003 to March 2004 and the particular influence on the coupon weight loss is not known.

The overall result for all works is that highly sensitive ER (electric resistance) measurements is suitable for surveillance of general corrosion velocity and the LOCOR cell (crevice corrosion current) is suitable for surveillance of local corrosion risks. Both techniques have reacted fast to environmental changes in the systems and make possible continuous corrosion monitoring.

Highly sensitive ER may be interpreted as electronic weight loss measurements that on-line trace continuous variations in corrosion velocity over very short periods (hours). In comparison, credible weight loss measurements in such systems have required a measuring period of minimum 6 months.

Changes in crevice corrosion current measured with the LOCOR cell have clearly indicated presence of local corrosion but the final value of the current can only carefully be converted to corrosion velocity due to the localised character. The LOCOR cell gives response to changes in the risk of local corrosion within minutes and the results can thus be compared directly to changes in operation.

Two electrochemical methods – linearly polarisation measuring (LPM) and electrochemical impedance spectroscopy (EIS) – have been applied primarily for mechanism studies. The LPR method is used for commercial continuous corrossions surveillance/detection, but it is not recommendable in district heating systems, as it has resulted in a strong tendency to overrate the corrosion velocity. In general, the EIS method has resulted in more credible corrosion velocities but analysing the data is demanding and the measuring period is too long (several days) to register sudden changes.

As regards the on-going corrosion situation at the works it should be stressed and concluded that the make-up water at the planned make-up water injections was deaerated which caused some local corrosion. Corrosion rates at 5-10 $\mu\text{m}/\text{year}$ were measured during make-up water dosage. The weight loss coupons had corroded during local corrosion, which is why the real corrosion rates are probably somewhat higher. During normal operation both the LOCOR cell and the ER measurements showed corrosion rates close to zero. The deaerator was out of order during the measuring period, which is why the oxygen content in the make-up water was very high. This is not usually the case. When the deaerater is in operation the oxygen content in the make-up water is reduced to approximately 100 ppb and it is presumed that the corrosion rate will be significantly lower.

Background

System: The system is a distribution system with approximately 12 km current newwork. Viborg Kraftvarme produce heat for the system. At an initiating visit to the site (on 28-09-2001) the flow temperature was 98,2°C the return flow temperature was 42,7 - 61,2 °C. The current network is made for a maximum pressure at 16 bar. The operating return flow pressure is around 2-3 bar.

Make-up water: Due to make-up water resale consumption varies from one year to the other. In 2000 the consumption was approximately 2000 m³ and 3000 m³ in 2001. Make-up water is produced centrally via a cation exchanger, succeeded by a RO-system in a series. The make-up water is deaerated through thermal (micro-bubble) aeration. The make-up water oxygen content is said to be approximately. 75 ppb (max 100 ppb). The make-up water is dosed in a return pipe before the accumulator tank. The 5 year-old accumulator tank is supplied with a steam pillow. Steam is supplied from separate steam generators. Only few problems have occurred when trying to keep the steam pillow intact.

Circulation water: The oxygen content is very low. (Measured by the works at <5 ppb) and the conductivity is at approximately µS/cm. No oxygen adhesives or other addition agents are applied. The pH-value is regulated by sodium hydroxide (lye).

Experience with corrosion and damages to the supply network: No experience with corrosion inside the pipes.

Test program

Test condition and location of bypass-unit Online measurements have been performed by the bypass-unit figure 1b, attached to the works' return pipeline approximately 1 metre after make-up water dosage, figure 1a. The maximum make-up water addition is stated to be 5,5 m³/h and the flow on the return pipeline is stated at 600 m³/h which corresponds to an ideal dilution of more than 100 times. The circulation in the bypass-unit is maintained by a mounted circulation pump that supplies approximately 7 m³/h (175 m³/a day).

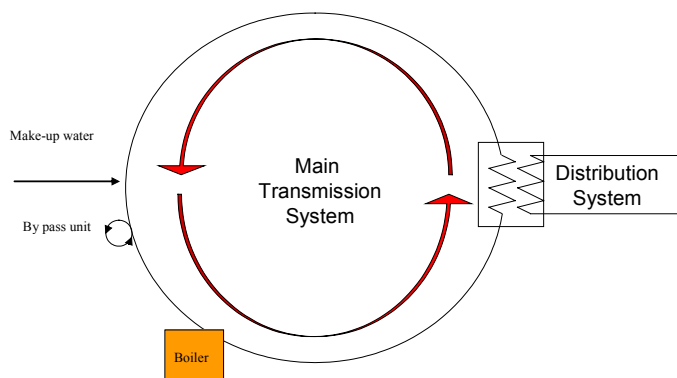


Figure 1a. Schematic presentation of the bypass unit's location. Pipeline network at Viborg.



Figure 1b. Photo of the bypass-unit with circulation pump before probe mountings.

Corrosion measurements have been made with 5 methods, to which has been applied a total of 4 different probe types: Weight loss coupons, ER-probes, LOCOR-CELL and three electrodes for LPR and EIS measurements. Measurements have been performed in the by-

pass units measuring chamber, where it is possible to mount probes, both at the bottom, the side and the top. Probes mounted at the bottom of the measuring chamber are partly sheltered from the water flow, see Figure 2.

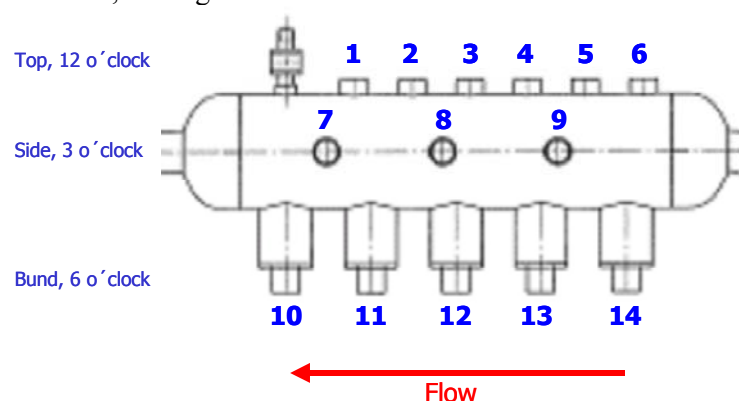


Figure 2. Probe locations in bypass-unit.

- 1: Weight loss coupon including steel disc for biofilm analysis
- 2: Empty
- 3: Three- electrode.
- 4: ER-probe
- 5: Weight loss coupon including steel disc for biofilm analysis
- 6: Weight loss coupon including steel disc for biofilm analysis
- 7: LOCOR-CELL
- 8: Thermo sensor
- 9: Empty
- 10: Weight loss coupon including steel disc for biofilm analysis
- 11: ER-probe with simulated deposits/crevice
- 12: Weight loss coupon including steel disc for biofilm analysis mounted in an extended bottom branch piece for simulation of a dead end
- 13: Three electrode
- 14: ER-probe.

Online measuring of water parameters (pH, conductivity and oxygen content) has been measured in a separate measuring panel, Figure 3, on an individual stream taken from the bypass-unit. Prior to measuring water parameters the individual stream is cooled in a sample cooler.

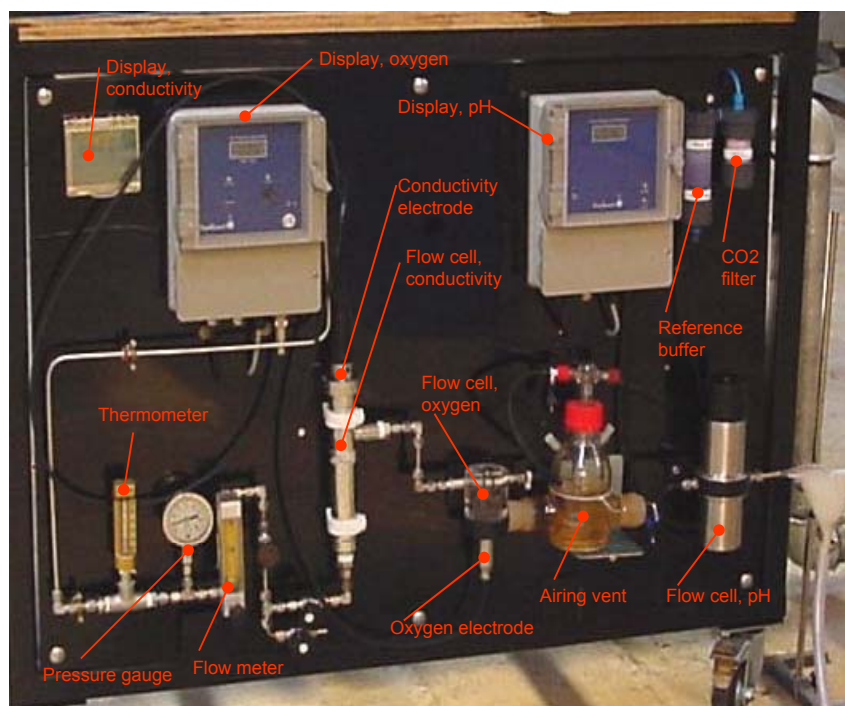


Figure 3. Photo of separate measuring panel for measuring water parameters.

All measurements (weight loss coupons excepted) are gathered on-line in a data logger. The Measurements can be traced centrally and at sight they may be included in the works' usual electronic surveillance.

Measuring results

Measuring results have been reproduced schematically below and are shown in curves in appendices 1-3. Photo of weight loss coupons are shown in appendix 4.

The system has a high pH, low conductivity and low oxygen content. The environment is stable, measured as temperature, conductivity and pH. Make-up water addition can be seen especially on the oxygen content, and this is also seen in the LOCOR cell response indicating a little increased local corrosion. ER and the electrochemical measurements indicate that such short-term oxygen peaks have not had great effect on the corrosion rate, which is somewhat increased at the end of the period. When considering the electrochemical methods EIS and the slow LPR seem reliable whereas the fast LPR overestimates the speed, but as even the slow LPR does not give a lineary measurement, the result is unreliable. The measurements show that too oxygenous make-up water result local corrosion and a slight increase in the general corrosion, but the effect is rapidly gone as the environment is otherwise stable. The three electrode probes are dark and semi-glossy, however with a few areas with somewhat blackish corrosion products.

Table 1. Schematic overview of measuring results.

Parameter	Measuring period	Normal operation	Event no. 2	Event no. 3	Event no. 4	Event no. 5	Event no. 6
	Day + night no.	0-27	12	17	21	25	25
Temperature, °C	0-27	47-52	50-51	50-51	48-49	48-49	47-48
Conductivity, µS/cm	0-27	~30	29-30	29-30	29-38	29-30	29-30
PH	0-27	9,5-9,7	9,6-9,7	~9,6	9,6-9,7	9,5-9,6	~9,5
Oxygen, ppb	0-27	0	~100	~100	~90	~100	~90
ER, µm/year probe 4, top	0-3/14-27	0/10	-	10, støj ¹			
ER, µm/year probe 11, bottom	14-27	2	-	10, støj ¹			
LOCOR-Cell, µm/year	0-27	0	5-6 ²				
LPR, µm/year probe 3, top	0/14/26	(1,5) ³ / 9 (1,7) ³ /(6,5) ₃	(6,5) ³				
LPR, µm/year probe 13, bottom	14/26	8,1	5,3 (1,7) ³				
EIS, µm/year probe 3, top	0	0,3	-	-	-	-	-
EIS, µm/year Probe 13, bottom	14	0,3	-	-	-	-	-
Weight loss, µm/year, probe 5, top	0-256	4	-	-	-	-	-
Weight loss, µm/year, probe 6, top	0-256	4	-	-	-	-	-
Weight loss µm/year, probe 10, bottom	0-256	3	-	-	-	-	-

Some noise that cannot be correlated with periods when the water is oxygenous. The results show clear lineary connection.

Tiny streams, negative at the beginning of the make-up water inlet. Variations clearly correspond to the make-up water

Slow LPR.

Table 2. Events during the test period.

Event no.	Description
0	Unit set-up, 19-06-2003
1	Start of online measurements, 06-08-2003 16:00, (time 0)
2	Day + night 12, 18-08-2003. Make-up water dosage 07:06-15:41
3	Day + night 17, 23-08-2003. Make-up water dosage 10:38-15:40
4	Day + night 21, 27-08-2003. Make-up water dosage 07:54-12:56
5	Day + night 25, 30-08-2003. Make-up water dosage 22:07-03:09
6	Day + night 25, 31-08-2003. Make-up water dosage 11:13-16:16
7	Day + night 26, 01-09-2003. End of online measurements
8	Weight loss coupon outlet 01-03-2004

Appendix 1.

Measurements of water parameters

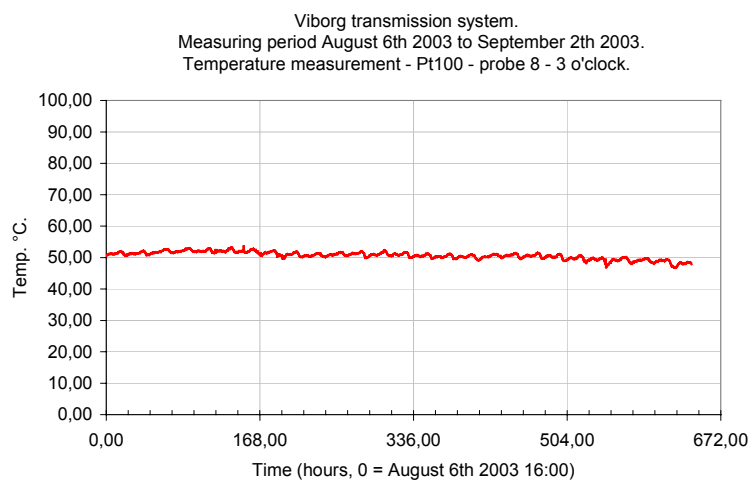


Figure 1. Circulating water temperature measured in the bypass-unit. Probe 8 – 3 o'clock.

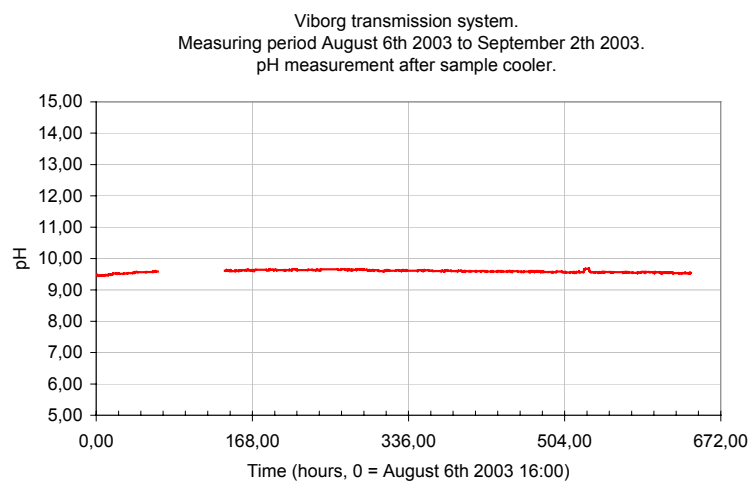


Figure 2. Circulating water pH-value measured in separate measuring panel after sample cooler.

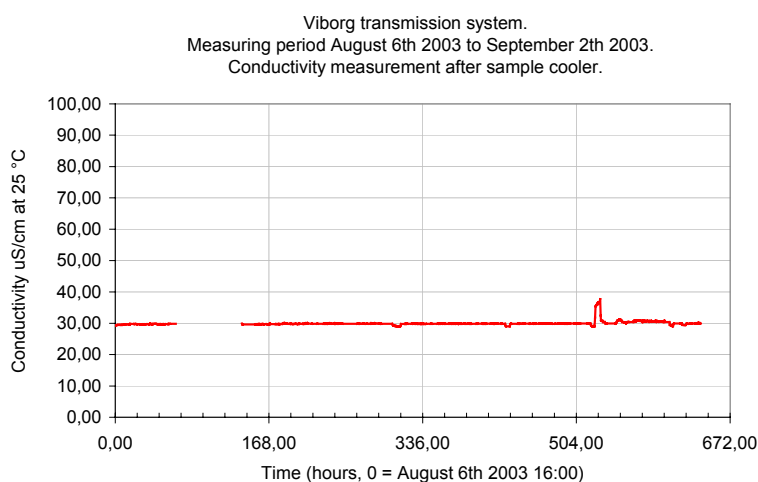


Figure 3. Circulating water conductivity measured in separate measuring panel after sample cooler.

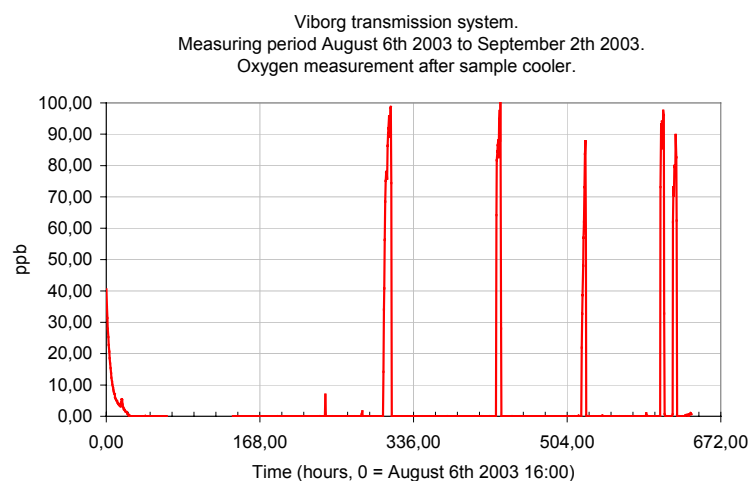


Figure 4. Circulating water oxygen content measured in separate measuring panel after sample cooler.

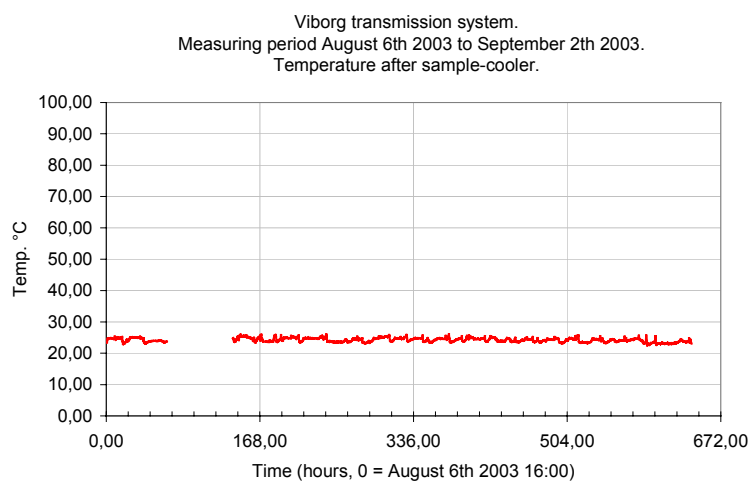


Figure 5. Temperature after sample cooler.

Appendix 2.

Corrosion measurements with ER-probes and LOCOR-CELL

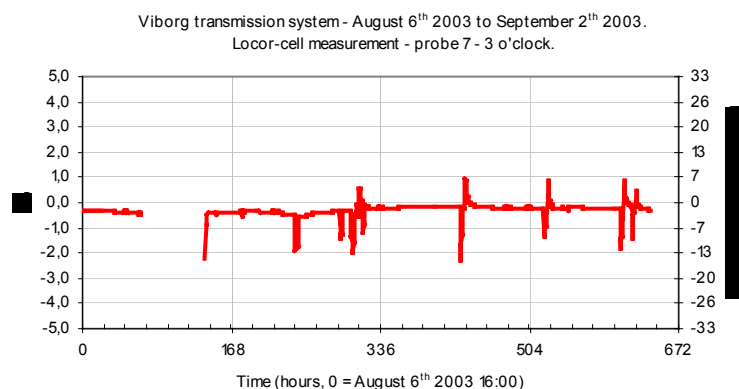


Figure 1. Measurements with LOCOR-CELL. Probe 7 – 3 o'clock.
The measured corrosion rates must be multiplied by a factor to compensate for local corrosion attacks on the anode.

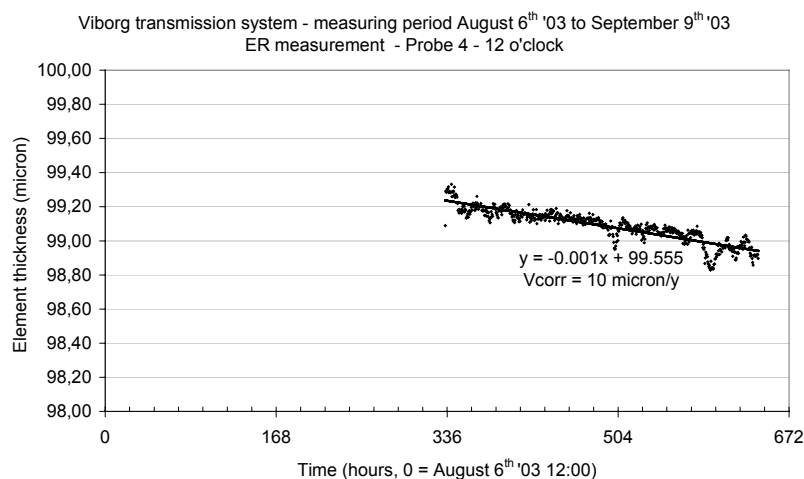


Figure 2. Measurements with ER-probe. Probe 4 – 12 o'clock.

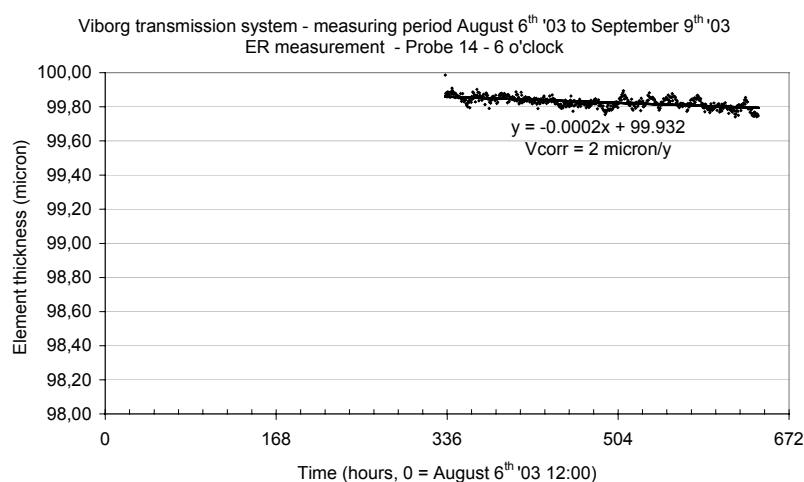


Figure 3. Measurements with covered ER-probe. Probe 14 – 6 o'clock.

Appendix 3. Corrosion measurements with three electrodes LPR and EIS

Viborg transmission system - August 6th 2003 to September 9th 2003
Electrochemical measurements - Probe 3 - 12 o'clock

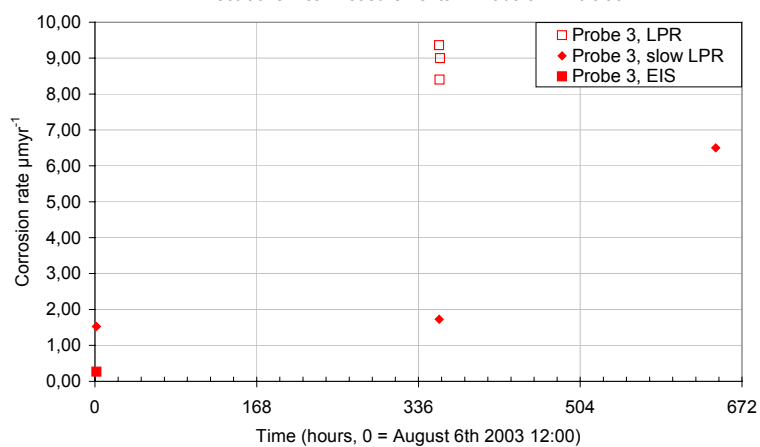


Figure 1. Probe 3 – 12 o'clock.

Viborg transmission system - August 6th 2003 to September 9th 2003
Electrochemical measurements - Probe 13 - 6 o'clock

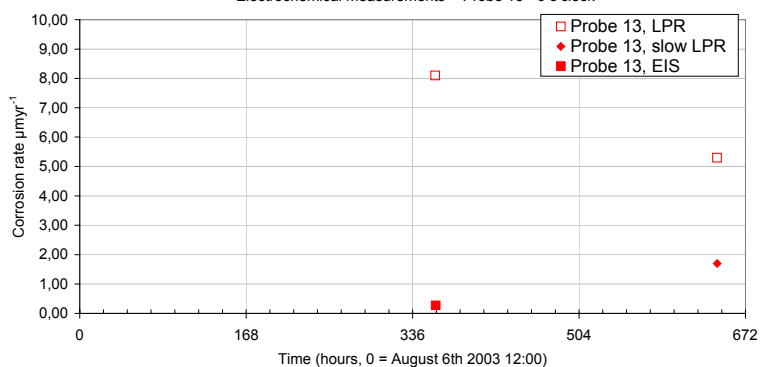


Figure 2. Probe 13 – 6 o'clock.

Photos of weight loss coupons

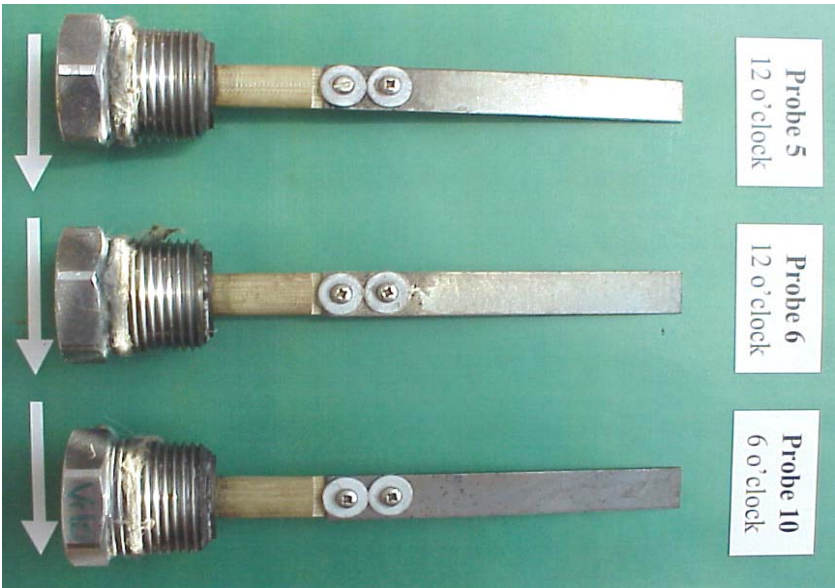


Photo 1. Overview of weight loss coupons probe 5 12 o'clock, probe 6 12 o'clock and probe 10 6 o'clock.



Photo 2. Overview of weight loss coupons probe 5 12 o'clock, probe 6 12 o'clock and probe 10 6 o'clock.



Photo 3. Detail of weight loss coupons. Seen from left probe 5 12 o'clock, probe 6 12 o'clock and probe 10 6 o'clock.

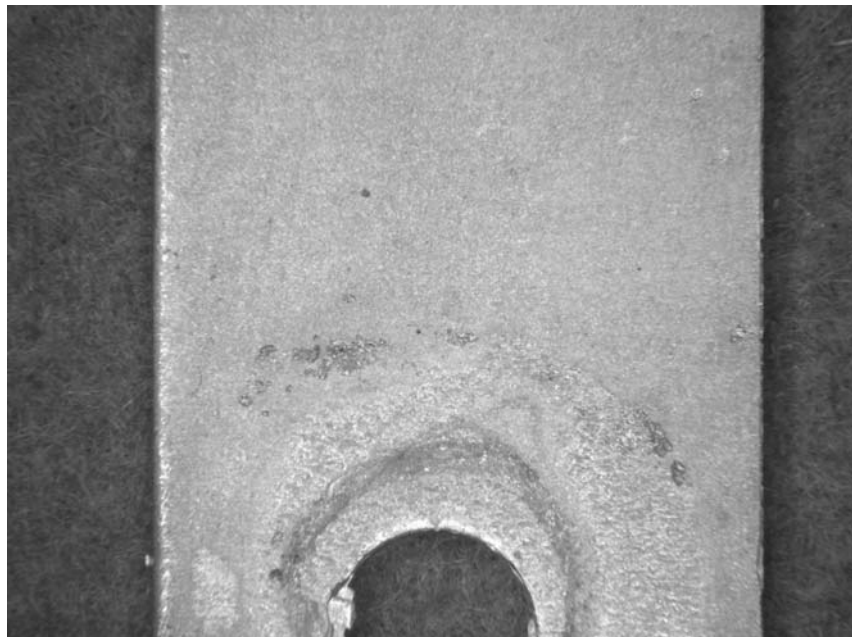


Photo 4. Detail of weight loss coupon probe 10 6 o'clock after cleansing. Approximately 6x enlargement.

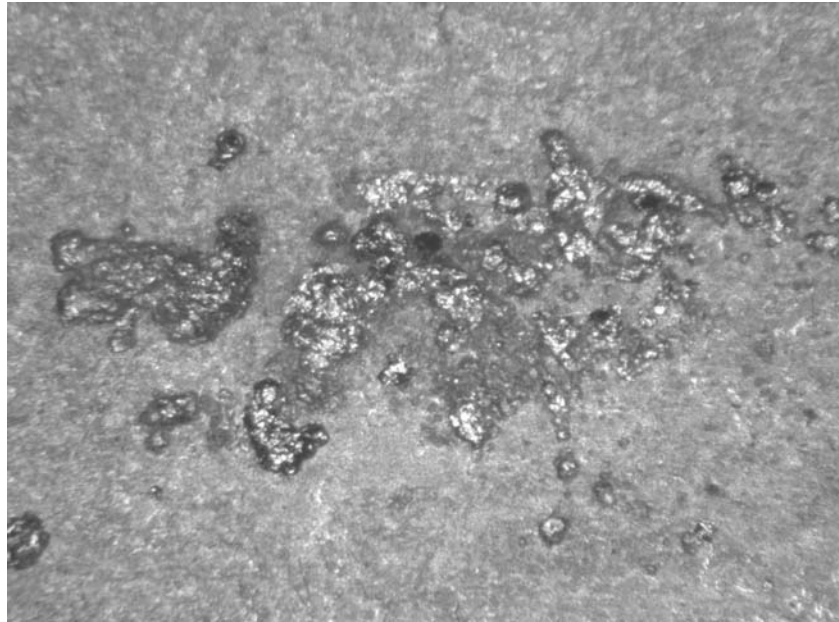


Photo 5. Detail of weight loss coupon probe 10 6 o'clock after cleansing. Approximately 50x enlargement.