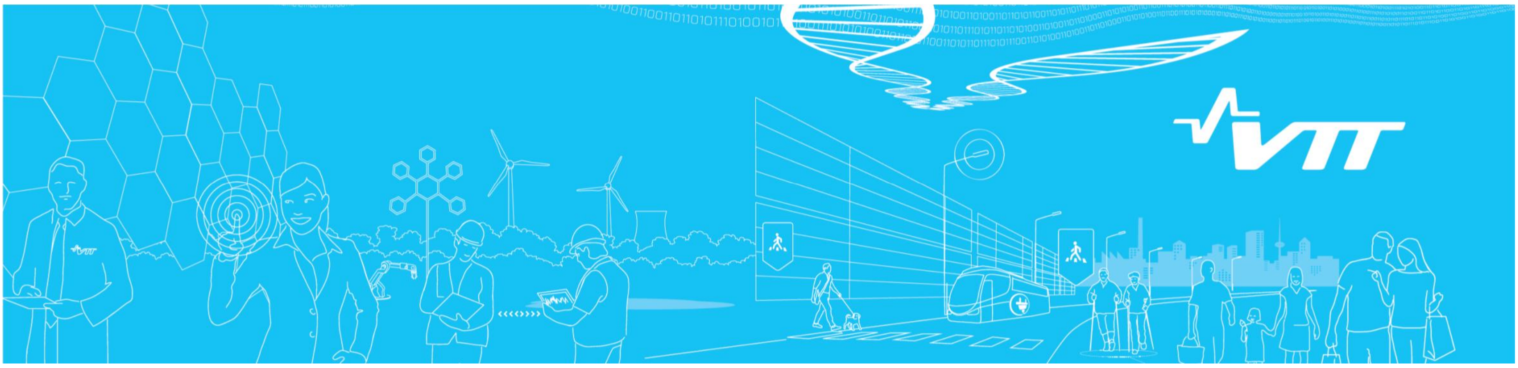

RESEARCH REPORT

VTT-R-02118-15

Properties and monitoring of precipitates and related corrosion

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Confidentiality: Public

Report's title

Properties and monitoring of organic and inorganic precipitates and related corrosion

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Summary

Severe organic fouling, inorganic scaling, and related corrosion in industrial water systems create great challenges, since they can potentially cause damage to the installation, which results in efficiency losses. Many fouling and scaling prevention measures (chemical treatments etc.) are utilised in process water systems, but from the environmental and economic point of view alternative ways and/or more efficient use of the existing methods are needed.

To be able to apply the optimised level of biofouling and inorganic scaling prevention to industrial water systems, the monitoring of deposit accumulation is in a key role. Detecting the type of deposits (organic or inorganic) is vital, and try-outs to tackle the separation have been made. Also detecting the localized corrosion related to scaling and fouling is important. Most methods are capable of detecting some properties (localized corrosion, deposit growth or different types of deposits) and function either off-line or on-line, but a method that could detect all at once, is not yet found. Therefore a monitoring system that is a combination of different methods could be potential. Different method combinations exist already (electrochemical impedance spectroscopy with ultrasonic technique, wire beam electrode method with sensing probes) and their applicability to scaling and fouling detection should be further explored.

Confidentiality	Public

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Preface

This literature review was performed during the summer and autumn of 2014 as a part of TEKES jointly-funded project “Finnish Metals and Engineering Competence Cluster - Breakthrough steels and applications: P1 Material challenges from emerging processes and applications”. The review goes through properties of organic and inorganic precipitates, and potential monitoring methods of organic and inorganic scaling, that haven’t earlier been studied in detail in literature review conducted at VTT. Also corrosion monitoring related to scaling and fouling is reviewed here.

Espoo 12.5.2015

Author

1. Introduction

Severe fouling and related corrosion in different industrial water systems, e.g. cooling water systems, create great challenges, since they can potentially reduce heat-transfer capability, increase maintenance costs, reduce plant availability, and contaminate process lines. Localized (e.g. pitting, crevice) corrosion, inorganic and organic scaling, and microbial fouling cause damage to the installation, which results in efficiency losses. Heat-transfer surfaces in cooling water systems are especially prone to fouling and associated corrosion damage. Because of the lower thermal conductivity of scales and deposits as compared to, for example, that of pipe materials, a thin scale film on heat transfer surfaces will greatly decrease the heat transfer process. Another problem concerning tubes is that a small change in the tube diameter significantly decreases the flow rate or increases the pressure drop across the heat transfer. Chemical treatments and many other fouling prevention procedures are utilised in process water systems, but from the environmental and economic point of view, alternative methods and/or more efficient use of the existing methods are needed. The possible over-and/or under-dosing of biocides and other fouling preventive substances can cause substantial harm. Therefore, monitoring solutions that may continuously and reliably be used to detect fouling and corrosion in the industrial water systems are most desired. [1-3]

Potential early warning solutions for industrial water systems need to provide information about the nature of the deposits formed and the related corrosion. Type of the deposit, its quantity, thickness, distribution, and the kinetics of formation and removal must be detected in order to assess the fouling potential. The corrosion monitoring data needs to specify what kind of corrosion takes place, and how fast does it proceed (i.e. the corrosion rate). In the most optimal case, fouling and corrosion monitoring information should be available on-line, in-situ, in real time, and non-destructively. Also suitability for computer-aided automatization is an important feature. [4] Goal of this literature review is to find out the properties of biofilms, organic and inorganic precipitates, and to reveal potential monitoring methods of organic and inorganic scaling, that have not earlier been covered by literature surveys conducted at VTT. [5]. In addition, scaling related corrosion monitoring methods are reviewed. Information on the development of new sensors for separation of biofouling and organic and inorganic scaling in the industrial water applications is also provided.

2. Organic and inorganic scaling

Organic and inorganic fouling is one of the major problems associated with especially heat exchanger operations. In this review fouling and scaling are used as synonyms to describe combinations of biofouling, deposit formation, and organic and inorganic scaling. Properties of fouling depend on the processes involved in their formation. In general, fouling is classified into five types: biological, corrosion, particulate, chemical reaction and crystallization fouling. The fouling accumulation may be considered as the result of several physical, chemical and biological processes: the transport of soluble and particulate components towards the installation surface, adsorption of this material to the surface, chemical and biological reactions and the detachment of deposit layer portions. High biological activity of different process waters promotes the biofilm growth on the heat transfer surfaces, affecting the cooling process. Chemicals such as chlorine dioxide, peracetic acid and quaternary ammonium, advanced oxidation processes, different toxic paints, and non-chemical treatments as UV radiation, ultrasound, thermal treatments and electric pulses have been studied as antifouling treatments. Currently, chlorine is the most widely used antifouling biocide in industrial heat exchangers due to its low cost and high effectiveness. However, there is an increasing environmental concern regarding the use of chlorine due to its high reactivity with natural organic matter in the water. The processes controlling fouling formation are very complex due to the variety of factors involved (e.g. water composition, microorganisms involved, materials, temperature, pH, flow rate) and their interactions. [6-7]

2.1 Inorganic species

Although many types of fouling takes place in the heat transfer equipment (heat exchangers, condensers, evaporators, cooling towers, boilers, and pipe walls), salt deposition is especially important type of fouling. The dissolved inorganic salts are normally present in the cooling fluid of the heat exchanger and their maximum concentration is limited to the saturation level. However, during heating or cooling periods, the super-saturation takes place in the dissolved inorganic salts while contributing to the fouling rate. As the heat exchanger tube wall temperature exceeds the corresponding saturation temperature of the salts dissolved, a crystal formation takes place on the surface of the wall. The crystallization starts especially at the nucleation sites such as scratches and pits, and often after induction period spread to cover the entire surface. However, by using selective tubes (for example titanium tubes) or selected tube surfaces (coated carbon tubes), this phenomenon is partially diminished and the rate of fouling may be reduced. The material of the tube influences also the fouling morphology and the spreading out. Therefore the investigation of fouling rate (affected by different tube materials) and coating becomes very important. [8]

The scale deposition mechanism is often described by a process that includes: dissolution of minerals, supersaturation, nucleation, precipitation, crystal growth, and finally scale deposition. The deposition mechanism is affected by many factors, for example fluid and surface temperature, flow velocity, pressure, and pH. The type of scales varies depending on the industry involved (i.e. chemistry of water) and the mineral content of available water. Most common inorganic fouling and scaling species in cooling water systems are calcium (calcium carbonate, calcium sulphate) and magnesium salts, silica, silicates and various metal salts and oxides. The common inorganic scales mentioned in the previous review [5] are presented in Table 1. Their physical properties, such as thermal and electric conductivities, are different than those of pure metals and therefore it is expected that for example electrochemical technologies can be used to distinguish specific fouling or scaling species.

One of the most studied scale is calcium carbonate $CaCO_3$. The solubility of calcium carbonate $CaCO_3$ in water decreases with increasing temperature and pH, whereas it also decreases with decreasing pressure. If the solubility of $CaCO_3$ decreases due to the condition changes in fluid, calcium and bicarbonate ions precipitate to form $CaCO_3$ crystals. Usually heat transfer surfaces are negatively charged (in solutions with pH higher than 7), so positively charged ions such as calcium and magnesium line up against heat transfer surfaces, which leads mineral ions to adhere to the heat transfer surfaces as $CaCO_3$ crystals. [3,5]

Table 1. Common inorganic scaling and biofouling organisms. [5]

Inorganic scaling			
Calcium & magnesium salts			
Calcium carbonate	Calcium phosphate	Calcium sulphate	
Metal oxides			
Iron-based scale	Manganese based scales	Zinc based scales	Silica scales
Biofouling			
Bacteria	Algae	Fungi	Biofilm

2.2 Organic species

Organic fouling can be composed of either living organisms (biofouling) or non- living organic substance. Biggest problem is usually bacteria-induced biofouling, which causes cooling system deterioration, loss of efficiency and high operating system expenses. When a surface is placed underwater it is coated almost immediately with a film of proteins, polypeptides, and lipids produced by aquatic organisms or derived from their waste products. Endemic bacteria settle on this film and produce slime (microfouling). The biofilm can act as a glue to attract silt and mud particles and such deposits further reduce heat transfer. Once a biofilm has formed, it passes through a sequence where certain species are replaced or supplemented over time. Some of the organisms settling are not microbial but the larvae of macroscopic species. If these larvae survive and grow, macrofouling is established. One currently rapidly spreading biofouling organism (especially over the Finnish Baltic Sea coastline) is a hydroid species *Cordylophora caspia* (Pallas), which forms colonies of dense, shaggy mats on the conduits, pipes and walls within the plant (Fig. 1). [9] The most common biofouling organisms are shown in Table 1. These include bacteria, algae, fungi, and biofilm, and their properties are reviewed by Vepsäläinen & Carpen [5].

Figure 1. Cordylophora caspia (Pallas). [9]

Most biofilms are mainly heterogeneous matrices of extracellular polymeric substances (EPS), with clusters made of cells and polymers, randomly distributed along a three-dimensional architecture and surrounded by water channels. Less than 5% of biofilms consists of actual micro-organisms, and the water content is about 90–99% of the total wet mass. The EPS has the largest contribution to biofouling, hence the chemical composition and morphology of EPS also has a great influence. The characterisation and understanding of EPS in biofilms, and the transparent exopolymers (TEP) involved in their development is still a particularly difficult task. TEPs are excreted by microbes and self-assembled to form independently suspended particles that are present in almost all aquatic environments. Due to their sticky nature they strongly influence the formation of biofilms, as well as contributing to membrane surface fouling. The TEP concentration has been directly linked to the rate of membrane fouling. [5,6,10,11]

Measurement of the degree of biofouling can be difficult and makes its control also challenging. Because of the heterogeneity of biofilms, properties may change dramatically from one point to another inside the matrix. Furthermore, the morphology and structure of a biofilm is likely to change as the biofilm ages. The biofilm is held to the surface of the membrane by a combination of hydrogen bonding, Van Der Waal's forces, and electrostatic and ionic interactions. It has been shown that alginate films behave in a more solid-like manner than liquid, which is surprising since the behaviour of biofilms is assumed to be more gel-like. The ionic concentration has a strong effect on the rheology of these films. It has been also reported that lower shear rates on the surface where the biofilm grows, causes it to become more "fluffy", making it easier to remove and reducing resistance to tangential flow. [5,6,10,11]

2.3 Interactions between organic and inorganic scale

Fouling is a complex phenomenon in industrial cooling systems since two or more different types of foulants may act simultaneous: soluble species and suspended particles, micro-organisms and corrosion products, etc. The different mechanisms involved in each type of fouling interact with each other giving rise to synergistic phenomena which are very difficult to predict. Inorganic particles are known to influence micro-organism behaviour, since they alter the physico-chemical properties of the environment where the microbial activities take place. Various clay species are known to stimulate bacterial metabolism and growth, and clay particles have been found to protect micro-organisms from the effects of some toxic compounds. Some researchers have suggested that this effect can be related to the reduction of the toxicity of the substances produced during metabolism through adsorption or inactivation. The adsorption of beneficial molecules (glucose) on the surfaces of clay particles has also been reported to have an important effect on the microorganism activity. Quantitative information is needed to relate the biological activities and the inorganic particles that promote biofouling. [6,12]

In the study by Tian et al. [12] the effects of silica, SiO_2, the most common inorganic particles in the treated sewage, on the biofouling of the heat exchanger were studied. Treated sewage source heat pump systems (TSSHPSs) are an effective way to recover waste energy for heating and cooling. However, the plate heat exchangers used in TSSHPS systems experience considerable fouling in practice. To investigate the effect of the inorganic particles on the biofouling of the system, the plate heat exchanger and the flow cells were exposed to the model fluids with SiO_2 particle concentrations of 1, 10 and 100 mg l^{-1}. *Bacillus subtilis* is present in the treated sewage. The results of the study showed that the SiO_2 particles influenced the biofilm development, further impacting the resulting heat transfer degradation. An increased biofouling mass was observed with increasing SiO_2 concentration, however, the highest organic substance level in the biofouling and the highest biofouling heat transfer resistance were achieved at intermediate SiO_2 particle concentrations. The inorganic particles led to expansion of the biofouling layer structure, which further affected the rate of biofouling build-up. The biofilms formed in the presence of inorganic particles were found to be physically more stable than those in the absence of particles. The biofouling heat transfer resistance was found to be more related to the biofouling layer micro-structure than the total mass. The biofouling microstructure also affected the biofouling build-up rate. The findings of this study provide a guide for biofouling development, which may lead to large improvements of the efficiencies of heat exchangers used with treated sewage. [12]

Rubio et al. [6] studied the progression of fouling in a condenser of a combined cycle power plant cooled by seawater, under actual operating conditions. Experiments of this study were carried out in a portable pilot plant designed to monitor the progression of fouling under similar conditions to those in the industrial heat exchanger. The pilot plant design was adapted to the different operating conditions required for in situ studies. The characterization of the removed fouling was performed in the laboratory by measuring the following parameters: 1) fouling wet volume, 2) mass of volatile and inert solids (gravimetric analysis), 3) layer thickness, calculated as the ratio between the wet volume and the inner surface area of the tube, 4) elemental composition of the fouling (C, H, N and S) by using an elemental analyser, and 5) metallic composition of the fouling, including the elements: Si, Al, Fe, Ca, K, Mg and Ti measured by X-ray fluorescence. The fouling progression was monitored inside the test tubes by the overall heat transfer resistance (R). The results revealed that the nature of the fouling was predominantly inorganic, containing over 70% of inorganic matter in all the studied cases. Organic matter was higher in the seasons of higher biological activity on the marine environment, spring and summer, and was lower in autumn and winter. The greatest percentage of organic matter in the fouling was obtained with the highest flow velocity and the organic matter decreased with the reduction in the cooling water flow velocity. While the percentage of inorganic carbon showed no major changes, the organic C, H, N and S rose their percentage as the flow velocity increased. The flow velocity also influenced the chemical composition of the fouling layer. Elements Si, Al, Ca and Fe showed different concentrations depending on the applied flow velocity. Fe can be integrated into the fouling by adsorption onto organic compounds. Therefore, a high amount of organic matter could enhance the absorption of Fe by the fouling layer. Elements K, Mg and Ti did not show differences between the different flow velocities tested. [6]

In the previous study [5], numerical values for a range of characteristics of various deposits and scales were collected (Table 2) in order to reveal differences between the various types of scaling. Properties such as thermal conductivity, electrical resistance/conductivity, permittivity (dielectric constant), and electrophoretic mobilities are shown in Table 2. Thermal conductivity indicates the ability of a material to conduct heat. By measuring heat flows of different deposits and scales, the identification of scales and deposits could be possible. However, making accurate heat flow measurements is rather difficult. [13] High electrical resistivity indicates low electrical conductivity and vice versa. In the simplest case electrical resistivity can be measured when a direct current passes through the sample. Common electrolytes vary considerably in resistivity (Fig. 2) for example from sea water (20 - 30 Ωcm) to granite rock (500 000 Ωcm). [14]

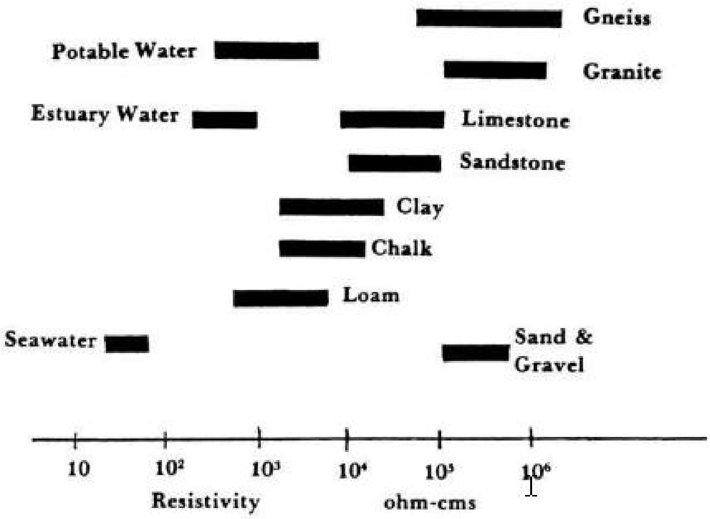
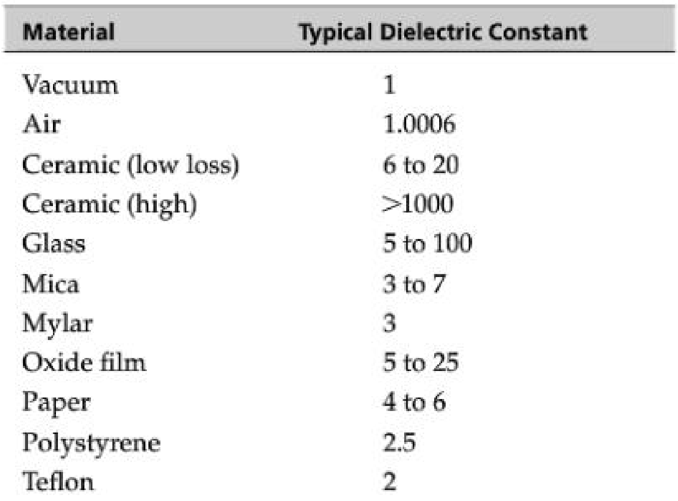


Figure 2. Example of electrical resistivity of different materials. [14]

Permittivity (also known as dielectric constant) is defined as a ratio of the electric displacement in a medium to the intensity of the electric field producing it. Permittivity of a substance or medium is generally expressed in terms of its relation to the permittivity of free space. Typical dielectric constants of different materials are shown in Fig. 3. [15] Electrophoretic mobility is the velocity of a charged particle expressed per unit field strength. Zeta potentials can be estimated from experimentally determined electrophoretic mobilities of particles. Zeta potential is the potential at the surface of shear of a charged particle; for macromolecular ions it is the potential at the surface of the hydrodynamic particles formed by such ion. [16]



Material	Typical Dielectric Constant
Vacuum	1
Air	1.0006
Ceramic (low loss)	6 to 20
Ceramic (high)	>1000
Glass	5 to 100
Mica	3 to 7
Mylar	3
Oxide film	5 to 25
Paper	4 to 6
Polystyrene	2.5
Teflon	2

Figure 3. Examples of dielectric constants (permittivity) of different materials. [15]

During this current study some additional data has been found to Table 2, and as a new feature the refractive index has been added to the table. Refractive index is defined as a numerical expression of the ratio of the speed of light in a vacuum to the speed of light in a test substance affected by factors such as free fatty acid, oxidation and heat treatment. Refractive index is used for identification of, and detection of impurities in volatile oils and other liquid substances. [17] As mentioned in [5] by Vepsäläinen & Carpen collecting the information is a challenging task since the data is very scattered and non-uniform in different sources.

Table 2. Some available data about the thermal conductivity, electrical resistivity, permittivity, electrophoretic mobilities, and refractive index of certain compounds and metals. [5] Previously obtained values are in black, and the new values in red (obtained from [18] and [19]).

Component	Thermal conductivity (λ) W/cmK	Electrical resistivity μΩcm	Permittivity/ dielectric constant, ε, rt	Electrophoretic mobilities (μm/s)(V/cm)$^{-1}$ in seawater	Refractive Index
$CaCO_3$	0.017…0.022		8.67 (ε_{11})	-1.19…-0.5	
$CaSO_4$*$2H_2O$	0.0025…0.005		5.10 (ε_{11})		
$MgSO_4$			8.2		
$MgCO_3$	0.15		8.1		
CuO		$6*10^{11}$	6 (ε_∞), 18.1		
Cu_2O		10^8	7.6		2.7
Fe_2O_3		$2*10^{10}$	12		2.4 – 3.01
Fe_3O_4	0.023…0.060	5200	20		1.43 – 1.5
MnO		$1*10^9$	12.8		2.16
MnO_2		$7*10^5$ - $3*10^9$	~10^4		
SiO_2	0.068-0.12	$5*10^6$ – $5*10^9$	4.42 (ε_{11})		1.44
Carbon steel	0.35-0.55	18			
SS 304	0.16	72			
SS 316	0.16	74			
Cast gray iron	0.52	67			
Inconel	0.17	103			
Al 2014	1.9- 2.5	3.4	1.9-2.5		
Cu (ETP)	3.9- 4.01	1.7	3.9-4.01		
Yellow brass	1.2- 1.09	6.4	1.2-1.09		
CuNi30	0.3	35	0.3		
Ti	1.8	43	1.8		
Zn	1.1	6	1.1		
Ni	0.9	10	0.9		
Biofilm+bacteria	0.007		0.007	-0.8, -1.0, -1.35	
Polysaccharide				-0.15	
H_2O	0.006	$1.0*10^8$	80 (at 20 °C)		1.33

3. Potential scaling and fouling monitoring methods

The early detection of inorganic and organic scaling and fouling is crucial in the prevention of further deposit or layer growth. Especially when considering biofouling, the prevention of bacterial attachment is important, since fully established biofilms are extremely resistant to chemical or physical treatments. The biofilm formation process begins with the initial attachment of microorganisms to solid surfaces. As the micro-organisms colonize the surface area, the attachment becomes irreversible and the attached growth of micro-organisms begins to form microcolony. This microcolony gradually matures to a highly structured biofilm. After the biofilm maturation, some cells in biofilm are detached, disperse planktonically, and colonize new sites to repeat the biofilm development. [10]

It is important to be aware of the actual parameters the monitoring systems refer to in order to interpret the data properly. Three levels of information can be identified: 1) systems which detect increase and decrease of material accumulating on a surface but cannot differentiate between biomass and other components of a deposit, 2) systems which provide biological information and distinguish between biotic and abiotic material, and 3) systems which provide detailed chemical information. [4] Main part of the potential methods for organic and inorganic scaling monitoring have been introduced in the earlier literature review [5], and are shown in Table 3. From these methods electrochemical impedance spectroscopy (EIS) and ultrasonic time-domain reflectometry (UTDR) were considered the most potential to be used as early warning systems. EIS measures impedance data of a system over a range of frequencies, when the frequency response of the system is revealed. In UTDR method the reflected ultra-sound signals are interpreted to indicate deposit thickness and density. Also monitors based on cyclic voltammetry and quartz crystal microbalance (QCM) techniques have been studied in many applications. Most of the current monitoring systems detect increase and decrease of material accumulating on surface, but cannot differentiate between organic and inorganic deposits. The next chapters will introduce additional monitoring methods that can be considered suitable for detecting scaling and fouling. [11,20-23]

Table 3. Organic and inorganic fouling and scaling monitoring technologies divided in three categories. [5]

Monitoring technologies	**Advantages**	**Disadvantages**
	Electrochemical methods	
Electrochemical impedance spectroscopy (EIS)	Suitable for monitoring the initial stages of biofilm formation	Unclear can it distinguish between different scales, water interferes the interpretation
Rotating disc electrode (RDE) systems	Rotating electrode system ensures that the mass transport to the surface is well defined and is controlled by adjusting the rotation speed, could be suitable for fast screening of antiscalants in laboratory	Can not be used as online system
Electrical (and thermal) resistance	Potential to measure the thickness of deposits on a surface in situ and in real time	Suitable only when one type of fouling or scaling occurs, gives only one result
Cyclic voltammetry	Bacteria attachment increased the current in cyclic voltammograms -> information on some specific properties of first bacteria attaching the surface.	Not suitable for online-measurements because potential changes significantly during the measurement which may affect properties of fouling layer.
Capacitance spectroscopy	Insensitive to changes in the bulk solution and has small dependence on temperature, online-monitoring tool which could	

	give qualitative information of composition of the fouling/scaling layer	
Acoustic methods		
Acoustic emission coupled with chronoamperometry	Suitable method for measuring inorganic scaling in situ	Unclear can it distinguish between different scales
Ultrasonic time domain reflectometry (UTDR)	Sensitive, non-destructive, potential in-situ monitoring tool, could be used for monitoring of several types of materials	Parameters are temperature dependent and thus temperature correction has to be included, unclear whether it could distinguish different types of scaling and fouling, not quantitative
Electrochemical quartz crystal microbalance (EQCM)	On-line, non-destructive, sensitive	No standard currently available, sensitive to pressure changes
Other methods		
Mechanotronic Surface Sensor (MSS)	Could distinguish different types of fouling and scaling layers from each other and give quantitative information	Not much studied

3.1 Electrochemical monitoring systems

Electrochemical techniques belong to the majority of scaling and fouling monitoring methods. They have many advantages in monitoring the microbial attachment and biofilm formation, since they are very sensitive to detect, and the data can be rapidly processed. In addition, they are environmental friendly and simple to operate because only small electrical energy is required to run the system. [10]

3.1.1 Electronic antifouling method (EAF)

Cho et al. [3] represent in their study the operating principle of the electronic antifouling (EAF) technology for preventing inorganic scaling (calcium carbonate) on water systems. The working principle of EAF is that it produces an oscillating electric field via Faraday’s law to provide necessary molecular mixing to dissolved mineral ions. Through improved collisions, they are converted to insoluble mineral crystals, a process called “controlled precipitation”. Therefore, the level of supersaturation of the hard water significantly decreases and new scale deposits are prevented. This means that the mineral crystals precipitate within the liquid, so that they are not able to precipitate on the pipe surfaces. Since fouling rate is the deposition rate minus the removal rate, the fouling rate can be negative when the EAF treatment eliminates the new scale deposits, suggesting that the existing scales can be removed over a period of time. The EAF seems an efficient way to neutralize the dissolved mineral ions and to prevent them from depositing on the heat transfer surface or pipe walls. The use of EAF is not only limited to calcium carbonate, but can also be used for other dissolved inorganic ions (e.g. Ca, Mg, Ba, Si, HCO_3^-, and SO_4^{2-}). The endurance of EAF treatment remains unknown, as well as the consequences of the precipitates within the water pipe. [3]

3.1.2 BIoGEORGE probe

BIoGEORGE probe, an on-line electrochemical biofilm monitor, has been developed to provide information on biofilm activity in cooling systems that are common in power plants and industrial facilities. The working principle of BIoGEORGE™ is based on a set of metal discs which act as electrodes: one half of the discs is polarised relative to the other for a short period of time (typically once a day for one hour). This applied polarization potential causes a current to flow between the electrodes. When a biofilm forms on the probe, it provides a path of a higher electrical conductivity for the applied current than the general medium in the system. An increase in the current flow over time is correlating with the amount of biofilm grown between the discs. Picture of BIoGEORGE is shown in Fig. 4.

The BIoGEORGE was tested in a waste disposal plant to describe the use of in biocide optimization. The plant is cooled by brackish water (salinity: 2.49 – 8.40 ‰, turbidity: 2.49 – 22.28 NTU, and pH: 7.50 – 8.40) in a once-through cooling water system. System piping was carbon steel, and the condenser tubes were made of titanium. The plant successfully applied sodium hypochlorite for control of macrofouling and microfouling. The probe was installed directly in the cooling water flow at the outlet of the condenser using a blind connection. Results showed that BIoGEORGE could be used effectively in online monitoring of biofilm formation. [22]

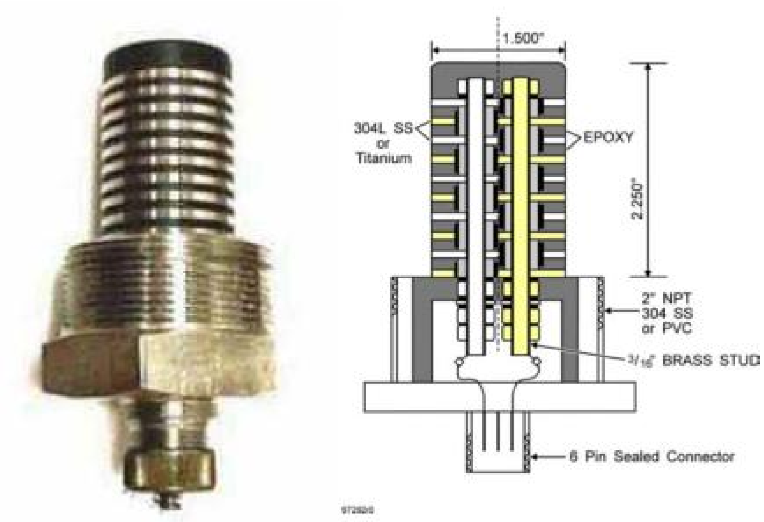


Figure 4. The BIoGEORGE probe. [22]

3.1.3 BIOX sensor

In a study by Cristiani et al. [24] an electrochemical on-line sensor BIOX was combined with chemical treatment using chlorine dioxide and mechanical cleaning using sponge balls to control microfouling in condensers in Italy. The BIOX system prevents macrofouling indirectly by preventing the microfouling build-up so that microfouling can't proceed to macrofouling. The BIOX system consists of a tubular electrochemical probe linked with specific hard/software to a computer (Fig. 5). Its response is correlated to the changes of electrochemical kinetic processes on metal surfaces induced by bacteria settlement or by oxidant agents. The probe registers the acceleration of the cathodic reaction of oxygen due to the biofilm growing on the probe surface and the cathodic reaction of the biocide oxidant present in the water. The probe detects oxidation rapidly, while the biofilm growth response time is relatively long. This is because of the time required for bacteria to colonise the complete surface of the electrodes. Therefore, when viewing the probe output responses over time, it is possible to distinguish the contribution of both phenomena under regular operating conditions. The system also includes a temperature sensor and flow meter. With the help of the BIOX system in the study, the dosage frequency of chlorine dioxide was possible to modify to an acceptable level. The BIOX usually show high sensitivity to the changes occurring at the electrode water interface, but the sensitivity as well as the working mode is at a fixed level. [9]

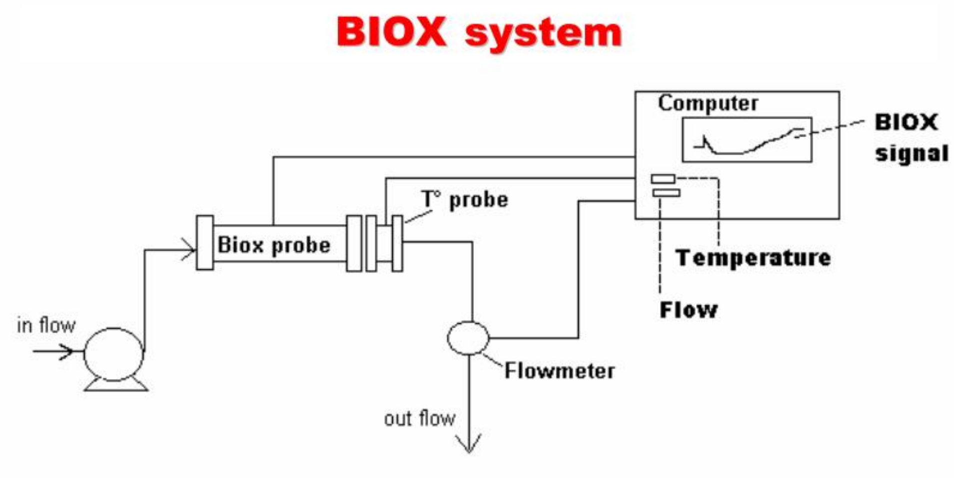


Figure 5. The working principle of BIOX system. [24]

3.1.4 Combined corrosion and fouling monitor (CFM500 Unit)

Conventional monitors for cooling water systems measure either corrosion or fouling separately. Fouling monitors alone are not able to indicate real-time corrosion activity beneath surface deposits. Scales and fouling have an immediate and significant impact on the surface corrosion condition, since they prevent uniform corrosion and promote instead localized attack, often in the form of pitting. Usually, corrosion information has been derived from destructive evaluation of heat exchanger tubes, weight loss coupons, and probes under nonheat flux conditions. In a study by Winters et al. [2] a monitoring instrument (CFM500 Unit) system has been developed for cooling water systems that measure corrosion and fouling simultaneously. The unit consists of state-of-the-art electrochemical techniques for corrosion assessment under in-plant service conditions. By using electrochemical noise measurement technology, the system is particularly sensitive to detecting localized corrosion beneath a fouled surface, a major and frequent mode of corrosion failure in the heat exchangers. Higher operating temperatures (up to 50°C) promote scaling and microbial growth, which interferes the access of a corrosion inhibitor to the heat transfer surfaces. Fouling tendency and the corrosion information is obtained by an integrated sensor system using four electrochemical techniques that make measurements simultaneously under heat flux: zero resistance ammetry (ZRA), electrochemical current noise (ECN), electrochemical potential noise (EPN), and linear polarization resistance (LPR). Zero resistance ammetry has been used conventionally to determine the galvanic current between two dissimilar electrodes, but may be also used to determine the current between two nominally identical electrodes. The EPN technique measures low-level random fluctuations of the corrosion potential between two nominally identical electrodes. The ECN measurement technique is similar to EPN, except that fluctuations in the coupling current between the two similar electrodes, typically less than 1 µA, are recorded and analyzed. During testing period the CFM500 unit was installed in the hot return line of a recirculating cooling water system fed with makeup water. Typical recirculating cooling water quality had pH of 8.5 - 9.0, alkalinity of 300 - 350 ppm as calcium carbonate $CaCO_3$, calcium of 280 - 320 ppm as $CaCO_3$, and total dissolved solids (TDS) of 800 - 1200 ppm resulting to a Langelier Saturation Index (LSI) between +1.9 and +2.4 at the estimated max. wall temperature of 43°C. The LSI value indicates $CaCO_3$ saturation, and a value close to 2 means that the water is scale-forming and for practical purposes noncorrosive. A LSI value close 0 indicates balanced situation with a chance of pitting corrosion, and a value of -2 indicates serious corrosion. [2,25]

According to the results the CFM500 unit gave real-time corrosion information on fouled heat transfer surfaces, and also the type of attack under deposits could be separated. The unit monitored the corrosion rate, local attack factor (pitting tendency), and the heat transfer resistance (HTR fouling tendency) on a graphical output. The corrosion reading from the

CFM500 can be used as an alarm for both corrosion and fouling changes because the corrosion readings are sensitive enough to be a good indication of minute changes in fouling behaviour. If operated under heavy fouling conditions, the CFM500 system is likely to indicate too high corrosion rates that are not representative of the heat exchanger unit. It was discovered that the LPRM probe did not detect corrosion truthfully, and lacked the ability to detect the localized and under-deposit corrosion. It was concluded that scaling and fouling accelerate localized corrosion on carbon steel heat exchanger tubing, and the rate of localized corrosion is higher than general corrosion in the system. [2,26]

3.1.5 Microbial fuel cells (MFC)

Several studies on electrical conductivity signals associated with microbial growth have suggested that microbial biofilms may be electrically conductive. Without a definitive value for biofilm electrical conductivity, the interpretations of changes in electrical conductivity in the presence of microbial activity is very difficult. Biofilms created by different bacterial species have distinct physical and chemical differences, and the local differences within biofilms are likely to cause differences in electrical conductivity as well. Recently, researchers have used electrochemical techniques, like microbial fuel cells (MFC), to investigate the biochemical properties of biofilms. In a study by Regberg et al. [27] the attempt is to grow a microbial biofilm in a controlled setting so that the biofilm's electrical properties can be measured. In this work MFC is used to study the biofilms that are composed of dissimilatory iron reducing bacteria.

In a MFC, current is generated by placing a working electrode either with a potentiostat or an oxygen cathode at a voltage similar to the redox potential of solid crystalline iron oxides (-0.2 V vs. Ag/AgCl reference electrode). When the MFC is in contact with dissimilatory iron reducing bacteria, they are observed to attach to the working electrode and utilize it as a terminal electron acceptor. Donating electrons to the working electrode creates electrical current that can be measured with the same potentiostat. The bulk conductivity of a fluid-saturated porous medium σ_b can often be described as a function of a fluid electrical conductivity σ_f with the following equation:

$$\sigma_b = a^{-1} \sigma_f \phi^m, \tag{1}$$

where Φ is the porosity, a and m are empirical factors related to extent of cementation and tortuosity, and σ_f is defined as:

$$\sigma_f = F \sum_j |Z_j| C_j \mu_j, \tag{2}$$

where F is Faraday's constant (C mol^{-1}), C_j is the concentration of species j in the pore fluid (mol m^{-3}), Z_j and Cj (m^2 (Vs)$^{-1}$) are the charge and electrical mobility of ion j. In the experimental part a series of abiotic, in vitro, and in vivo batch experiments were conducted to test the effect of iron oxide reduction on σ_f with as few reactions and variables as possible. One of the most advantageous aspect of using a MFC is the ability to precisely locate the biofilm in space.

The results show that the experiments using electrochemical methods to grow and maintain microbial biofilms were effective with iron-reducing bacteria. The measurements of changes in electrical conductivity were possible to obtain as Geobacter biofilms grew and decayed. In the experiments, a minimum conductivity value was measured for the biofilms, though the measured values were quite low compared to the expected values by previous studies (biofilms growing in MFCs must have an electrical conductivity > 0.05 S/m). Reason for this could be that the measured values might have been taken at a point directly above the biofilm instead at the biofilm. Therefore, the electrical conductivity represent a minimum value for biofilm conductivity. This work also demonstrated that measurements of σ_b and flow rate, combined with a few direct chemical measurements, can be used to quantify biogeochemical reaction rates in controlled laboratory situations and may be able to detect the presence of biofilms. [27-28]

3.1.6 Scanning probes

Paper by Tan et al. [29-30] presents an overview of scanning probe techniques for characterizing inhomogeneities in various forms of organic surface films including organic coatings, corrosion inhibitor and anti-corrosion oil films. The mentioned scanning probe techniques are presented in Table 4. Each scanning probe technique has its advantages and limitations, for this reason, different techniques are often combined and applied in a synergistic manner. For example SECM and AFM commonly operate in a relatively specific and localized area under strictly controlled experimental conditions, and therefore the successful imaging is rather difficult to conduct in experiments. Another common issue regarding scanning probe techniques is that scanning an electrode surface at close proximity could disturb local electrochemical reactions. The scanning probe techniques are able to study localized corrosion, but are unable to scan corrosion occurring under solid deposits. [29-30]

Table 4. The mentioned scanning probe techniques by Tan et al. [30-33]

Scanning probe technique	Advantages	Disadvantages
AFM (atomic force microscopy)	Surface features can be measured and mapped for example as height profile	Presence of contaminants on the probe → effect on imaging resolution, probe-sample contact area is a limit to resolution
SKP (scanning Kelvin probe)	Non-invasive, no-contact vibrating capacitor technique. Can be used to investigate localized variations in coatings by mapping e.g. Volta potential or electrochemical activity.	Resolution is not high enough for probing the submicroscopic coating defects, experimental data could be difficult to interpret
SKPFM (scanning Kelvin probe force microscopy)	Combines SKP and AFM functions, can be used to gain more information about the microscopic and submicroscopic processes occurring at coatings	Resolution is strongly dependent on the distance between tip and the coating/metal interface, Probe results vary due to differences in the oxide covering them, or contaminants deposited on the tip
SRET (scanning reference electrode technique)	Can detect inhomogeneities in coatings, and localized corrosion damages by measuring ionic currents flowing in the electrolyte phase over a corroding metal surface	
SVET (scanning vibrating electrode technique)	Direct measure of the electric field, useful technique for differentiating (in situ and in real time) corrosion activity of metals immersed in conducting electrolytes	Probe system depends upon several parameters, related to both the machine settings and solution conditions
LEIS (local electrochemical impedance spectroscopy)	A powerful tool to investigate localized corrosion on bare metal surfaces and on coated alloys	Necessary to obtain more information from local impedance spectra
SECM (scanning electrochemical microscopy)	High-resolution chemical concentration maps of corroding metal surfaces.	Somewhat limited (typically several microns) spatial resolution

3.1.7 Coupled multi-electrode array sensor (CMAS) and wire beam electrode array (WBE)

CMAS is a coupled multi-electrode (also known as microelectrode) array sensor, which consists of multiple miniature electrodes that are the active sensing element of the sensor. These miniature electrodes are made of metals identical to the material of construction of the process, and whose corrosion rate is of monitoring interest, and are coupled to a common joint through independent resistors. Thus, each electrode represents part of a corroding metal if the sensor is in a corrosive environment. In a localized corrosion environment, anodic currents flow into the more corroding electrode and cathodic currents flow out of the less or non-corroding electrodes. Such currents are measured from the voltages across the resistors and are used as the signals for non-uniform corrosion (including localized corrosion). For quantitative corrosion rate measurements, CMAS probes are more sensitive to the effect of crevices formed between the sensing electrode and the insulator than the other types of electrochemical probes because of the small electrodes used. CMAS can be used in solutions of higher resistance, because the microelectrodes are closely packed, so the influence of solution resistance is decreased. However the close proximity of the electrodes makes them vulnerable to short circuiting by corrosion products. No standard is currently available to provide guidelines for using this technique, as is the case with many other techniques mentioned in this review. [34-36]

Tan et al. [30] studied an electrochemically integrated multi-electrode array system to understand in-homogeneities in surface films and localized under-film corrosion. The system used was called the wire beam electrode (WBE) method, one modification of the CMAS method. The WBE is a non-scanning probe technique that is able to visualize the processes of localized corrosion under a coating or an inhibitor film by measuring parameters from local areas of a working electrode surface, such as local resistance, corrosion potential and galvanic current, providing spatial and temporal information on under-film localized corrosion. Porosities, cracks and non-uniform molecular crosslink in organic coating films have long been recognized to significantly influence the anti-corrosion performance of coating systems by creating degradation-susceptible regions. The WBE method involves subdividing an area of a coated surface into many small sections and measuring the electrochemical properties of each part by individual sensors. An example of the result received from the individual sensors is shown in Fig. 6, where non-uniform distribution of galvanic current density over a coated WBE surface was mapped. The main anode and cathode areas can be distinguished. According to the results the applicability of the WBE method in mapping in-homogeneities over coated metal surfaces by detecting coating electrical resistances and potential differences is very good. The WBE could be applied in conjunction with scanning probe techniques (the previous chapter) in order to gain more detailed understanding on the different phases of localized corrosion under organic surface films. For instance it may be possible to correlate WBE galvanic current density, coating resistance or potential distribution maps with Volta potential profile measured by the Scanning Kelvin Probe. [30]

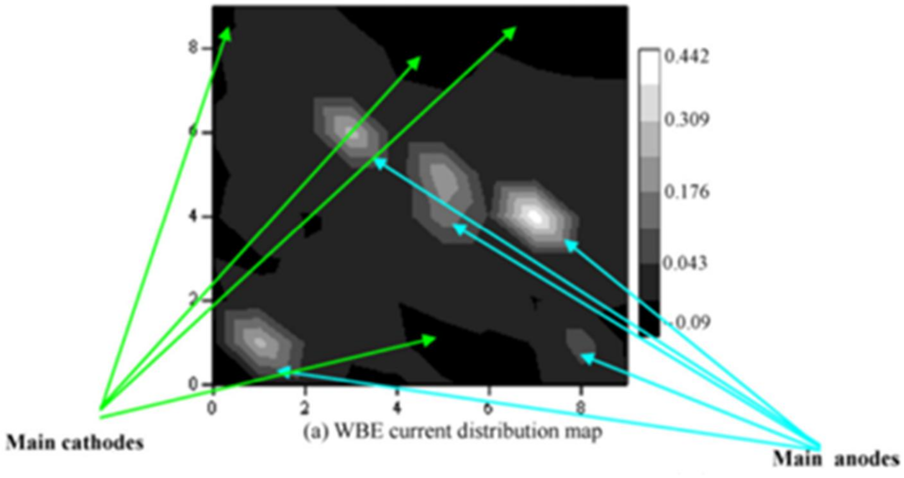


Figure 6. WBE galvanic current density (mA/cm^2) distribution maps measured from a mild steel WBE surface coated with a WD-40 oil layer and exposed to the Evans solution (0.017 mol NaCl, 0.008 mol Na_2CO_3 in 1000 ml deionized water) for 38 h. [30]

3.2 Methods based on light reflection

3.2.1 Focused beam reflectance measurement (FBRM)

In the study by Nasser et al. [37] a laboratory online monitoring technique to indicate mineral scale agglomeration was developed. The method is based on Focused Beam Reflectance Measurement (FBRM) technique (Mettler Toledo), which measures the chord size distribution of crystals in solution. It is based on the light reflection where the FBRM probe detects and transforms the reflected light into an electronic signal. This method can provide the induction time of starting agglomeration, and is capable of detecting the changes in very small time intervals. The experimental set-up consists of a beaker placed on a hot plate with FBRM immersed at an angle along with a temperature probe. The sensors were connected to a PC to record the number of crystals and temperature of the solution in every 2 s. The number of particles was detected in 2 mm range at the FBRM probe in the solution beaker. The calcium carbonate formed during precipitation deposits on the window of the FBRM probe, thus the probe was cleaned regularly during measurement. The number of crystals deposited on the surface of the probe can be determined by the difference in number of chords measured before cleaning and after cleaning.

The results showed that the calcium carbonate precipitation and deposition rates could be obtained from the FBRM. The method seemed useful in determining the minimum precipitation inhibitor concentration and to screen various types of inhibitors for the selection. The presence of inhibitor delays the agglomeration and affects the deposition of calcium carbonate. SEM images revealed that the mechanism of inhibition might be the surface adsorption or distortion of inhibitor molecules on the growing calcium carbonate crystals. The possibility of the adsorption of inhibitor molecules on the crystal surface is significant in the inhibition of crystal growth. The results of the method were validated by comparing the results with results obtained from conventional offline technique. [37]

3.2.2 Photointerrupt sensor array

A study by Tung et al. [38] focused on testing of a photointerrupt sensor for real-time online monitoring of a fouling-cake thickness growth during a submerged membrane filtration process. The working principle of the sensor is that when an object comes close to the sensor, the light from an emitter is reflected from the surface of the object into the collector. The idea of the sensor is shown in Fig. 7. In the experiment a membrane module with a filtration area of 0.325 m^2 and the photointerrupt sensor array were both mounted inside a suspension tank. The photointerrupt sensor was able to slide/move steadily and freely in the upward and downward directions to monitor the cake thickness at different positions. PTFE and PVDF membranes in water and in a TiO_2 slurry medium were studied.

The results show that the output voltage signal response of the photo sensor was a function of the surrounding medium and the distance between the sensor and membrane. The effect of increasing particle concentration on sensor output voltage signal was more dominant at long distances (>1.5 mm) and was almost negligible at shorter distances (<1.0 mm). At high particle concentrations, the sensitivity of the sensor was reduced as the distance between the sensor and membrane increased. The output voltage signal response of all sensors was higher for the PTFE membrane than for the PVDF membrane in both water and the slurry medium. The average fouling- cake-layer thickness increased proportionally with time during the initial period (0–150 min) due to the rapid deposition of TiO_2 particles on the membrane surface, after which the growth rate of fouling decreased. It seems that the application of photointerrupt sensors can be effectively used to investigate the fouling formations of submerged membrane filtration systems under different conditions. However, no info is received on the layer properties of the studied material. [38]

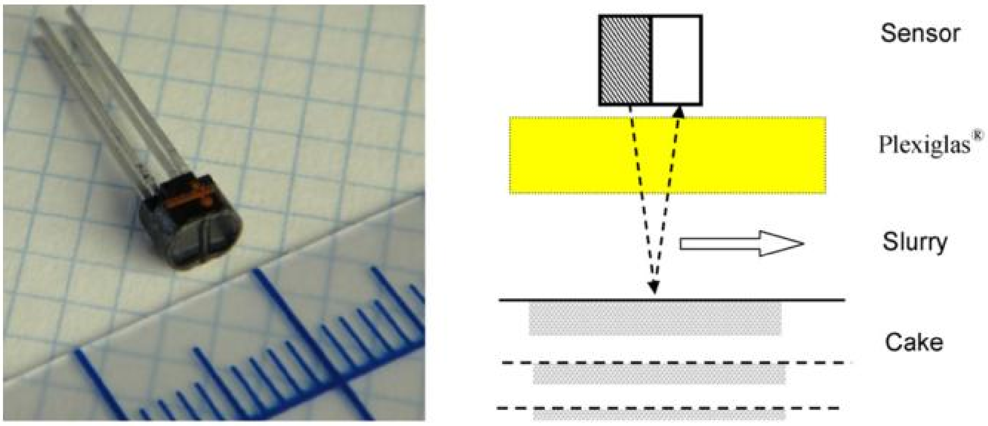


Figure 7. The working principle of the photointerrupt sensor used for the measurement of growing cake thickness on a membrane surface during the filtration of a particulate suspension. [38]

3.2.3 LED photointerrupt sensor for dynamic monitoring

In a study by Chen et al. [39] an in situ fouling layer thickness measurement device with integrated online dynamic analysis capability to provide real-time information of the fouling layer structure for membrane filtration processes is proposed. The monitor consists of a LED photointerrupt sensor. This monitoring technique has preliminarily been demonstrated for water treatment microfiltration processes using a single photointerrupt sensor. In the experiments the sensor was installed in front of the filter chamber to measure the growing thickness of the fouling layer. The increase of the weight of filtrate was detected by a load cell and recorded on a laptop. According to the results the fouling layer thickness variation and a dynamic analysis procedure based on mass and force balances of particulate deposition on the membrane surface can be used to study the fouling layer structure in a water treatment membrane process. In addition, the water quality during the membrane filtration process can be monitored. [39]

3.3 Other methods

3.3.1 Differential turbidity measurement (DTM) and pressure drop (PD)

Paper mill process waters (as well as waters in waste water treatment plants, in sediments, soils and surface waters) provide conditions for a rapid growth of micro-organisms. In this study an online monitoring method by Klahre et al. [23] was developed based on differential turbidity measurement (DTM). The basic idea of the DTM is to use an effect which otherwise interferes with turbidity measurements: formation of a deposit on the window of a turbidity measurement device. If two identical devices are applied in the same system, one of them continuously cleaned, the differential signal originates exclusively from the fouling layer on the optical window. DTM is based on optical properties of the deposits and indicates the increase of reflecting material on the optical window (Fig. 8). As reference technique, automatic pressure drop (PD) measurement was used in the experiment. The idea of PD is based on the increase of pressure drop caused by viscoelastic biofilms (decrease in tube diameter or increase in surface roughness). This is however, difficult to calibrate.

Both DTM and PD proved to be useful for measurement of deposit formation on-line in the side stream of a paper machine whitewater circuit. With these methods the efficiency of chemical cleaning procedures and bacteriostatic compounds could be demonstrated. Optical methods using visible light to record the degree of fouling in a process water medium require little space and servicing. However, a direct correlation between the reflection in DTM and biomass is not yet established. Optical methods are also very sensitive to color changes in the medium. Both PD and DTM refer indifferently to deposits, and do not provide information on the fouling type. [23]

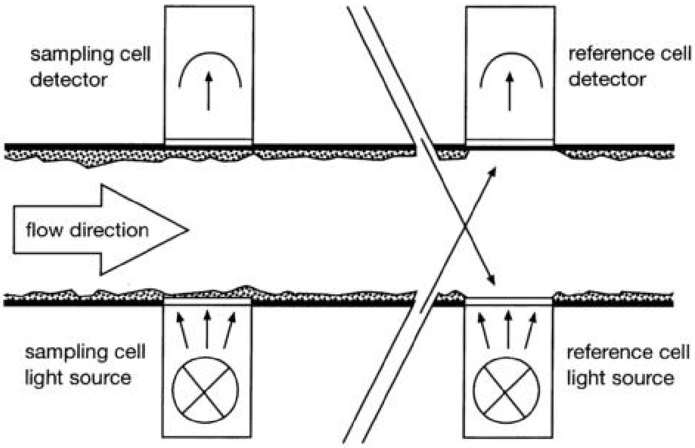


Figure 8. Idea of differential turbidity measurement device. [23]

3.3.2 Fluorescent dyes & CLSM

In practice different kinds of scales do not occur separately, but more or less mixed, influencing each other to a yet unknown extent. Spettman et al. [40] studied separation of organic and inorganic scales by using fluorescently labelled foulants. The generation of deposits was performed on polycarbonate microfiltration (MF) membranes and polyethersulfone ultrafiltration (UF) membranes. Microbial deposits were gathered by filtering tap water for 22 h through membranes. The studied foulants were: 1) drinking-water bacteria stained with nucleic acid-specific dyes (biofouling), 2) synthetic clay mineral laponite stained with rhodamine 6G (inorganic particle fouling) and 3) fluorescently labelled polystyrene microspheres (organic particle fouling). Single foulants in these mixed deposits could be visualised separately by confocal laser scanning microscopy (CLSM), which in combination with image analysis could deliver 3D pictures of the complete deposits. The CLSM is often used in the identification of specific components and the morphology of fouling layers. By using fluorescent dyes the different cleaning methods were able to be compared with each other and then find out which foulants were removed during cleaning process. However, the discrimination of the fluorescence signals of some molecules can be difficult to identify, in particular in the presence of quenching substances. One problem is also the suitability of this method for online applications. The CLSM only provides analysis of a small area (0.05 mm^2), so multiple samples are often required. The fouled areas have generally (especially in biofouling) large non-uniformity, which means that the sampling process has a great effect on the data accuracy. The CLSM and other fluorescence microscopy methods deeply rely on correct selection of staining compounds. [4,11,40]

3.3.3 FTIR-ATR spectroscopy

A method presented by Flemming et al. [4] is based on FTIR-ATR-spectroscopy in a flow-through cell. The spectrum of medium infra-red has proven to be the most indicative for biological material. The studied system is composed of an IR-transparent crystal of zinc selenide or germanium which is fixed in a flow-through cell. The attenuated total reflection (ATR) spectroscopy mode allows one to specifically receive the signals of material depositing on the ATR crystal because the IR beam penetrates the medium it is embedded in only into a maximum depth of 1–2 µm. Such systems could distinguish and identify abiotic and biotic material which attaches to the crystal surface. [4]

4. Localized corrosion monitoring

Monitoring methods of scaling and fouling are closely linked to corrosion monitoring methods. In some cases the monitors developed for corrosion monitoring can be used for scaling and fouling monitoring and vice versa. Especially localized corrosion, which is linked to under deposit corrosion and corrosion under demanding environments, is often consequence of scaling and fouling, and the processes feed each other. Therefore also some of the localized corrosion monitor methods are studied here. Methods that have been mentioned in the previous chapters are not mentioned here again.

Localized corrosion is the accelerated attack of a passive metal in a corrosive environment at discrete sites where the otherwise protective passive film has broken down. Common forms of localized corrosion include pitting, crevice corrosion, intergranular corrosion, stress-corrosion cracking, and exfoliation corrosion (a form of intergranular corrosion). Pitting corrosion can be divided into a sequence of steps: 1) initiation by the breakdown of the passive film, 2) metastable growth of small pits on, 3) stable growth of localized corrosion sites that can grow quite large, and 4) repassivation or termination of the attack (if conditions permit). Pitting corrosion is known to initiate above a critical potential and repassivate below another, lower potential. Once initiated, the attack is stabilized by the localized development of aggressive conditions as the result of metal cation hydrolysis and Cl^- migration. The exact susceptibility of sites for film breakdown and the ability of other sites to sustain cathodic reactions depend on details of the surface film properties that are not well understood. Localized corrosion for metal components is usually the major concern in chemical plants or nuclear power plants because localized corrosion is difficult to detect at an early enough stage to mitigate it. Once initiated, localized corrosion can propagate rapidly and result in either component failures (such as through wall penetrations) or trigger other modes of failures, such as stress-corrosion cracking. [35,41,42]

4.1 Common methods for localized corrosion monitoring

The most traditional localized corrosion monitoring methods and their characteristics are listed in Table 5. Some of the localized corrosion monitoring methods are suitable for monitoring many forms of corrosion, but several are applicable only to specific types of corrosion. On-line monitoring methods determine the corrosion rate repeatedly while the experiment is in progress because they don’t change the state of metal. On-line methods can be further divided into continuous and frequent. Offline techniques determine the corrosion rate after the specimen has been retrieved from the test. Destructive methods can be used in measuring only once, because they change the state of the specimen during the measurement. [34,43] The methods mentioned in the Table 5 are shortly described below.

Table 5. Existing corrosion monitoring methods for localized corrosion. [1,34,44]

Method	Advantages	Disadvantages
Weight loss coupons	Low cost, reliable, versatile	Slow, offline, destructive, corrosion rate only for general corrosion
UT (ultrasonic technique)	Non-destructive, non-intrusive, online	Accuracy depends on many factors
PP/CP (potentiodynamic/cyclic polarization)	Indicative of pitting and crevice corrosion, online	Destructive, complex, requires careful and informed interpretation
EQCM (electrochemical quartz crystal microbalance)	On-line, non-destructive, sensivite	No standard currently available, sensitive to pressure changes
ZRA (zero-resistance ammeter)	On-line, non-destructive, simple, can be used in high pressure systems	Usually only qualitative data on corrosion
EN (electrochemical noise)	Non-destructive, online, measurements can be made in a wide range of environmental resistivity	Complex, expensive, need for specialized knowledge, no quantitative data on corrosion
FSM/EFM (field signature method/ electrical field mapping)	Non-destructive, non-intrusive, online, large areas of components can be monitored, sensitive	High cost, requirement for specialized data interpretation, high temperature use, does not distinguish external or internal defects

4.1.1 Weight loss coupons

Weight loss coupons are metal samples that are exposed to the corrosion environment to establish the corrosion rate. They are withdrawn from the plant or from the studied environment at certain intervals and the corrosion rate is determined by gravimetric means, i.e., weighing the coupon before and after the exposure following the removal of the corrosion products. Use of weight loss coupons is very common in monitoring of general, localized and erosion corrosion. Inserting and withdrawing the coupons, especially the ones operating at higher temperature and/or higher pressure, requires sophisticated equipment. When using mass loss coupons it is important to place them properly inside the vessel at a location where the conditions are most severe to give a meaningful representation. [1,34]

4.1.2 Ultrasonic technique (UT)

The ultrasonic technique (UT) is a structural inspection technique to determine a general wall thinning due to general corrosion, erosion, and localized corrosion. The UT measures the thickness of solid materials. During UT inspection, a piezoelectric crystal (commonly known as a transducer) is placed on the object to send a time- wave through it. To transmit the time-wave between the transducer and the object a liquid medium is placed between them. The transducer oscillates and sends the wave across the material. In principle, UT can detect wall losses of 0.025 mm when the transducer is accurately placed and the process is accurately controlled. The measurement accuracy depends on several factors, including the variations of sound velocity in different metals, temperature variations in the substrate, and discrimination of the acoustic reflections. [34]

4.1.3 Potentiodynamic polarization (PP)

Potentiodynamic polarization (PP) is a probe method to monitor general and localized corrosion. Using the same set-up as for LPR measurement, the potential is scanned first in the anodic direction and then the direction of scan is reversed. The pitting tendency is obtained from the hysteresis plot. Cyclic polarization (CP) is a variation of the potentiodynamic technique in which the potential is scanned in the noble (positive) direction, then the current is monitored continuously until it reaches e.g. 5 mA, at which point the scan direction is reversed (scanned in the active, i.e. negative, direction), until the hysteresis loop completes (the current in the reverse scan is lower than that of the forward scan) or until the corrosion potential is reached. The potential at which the anodic current increases rapidly during the forward scan is taken as the indication of initiation of localized corrosion. The CP doesn’t give information on the rates of localized corrosion. [34,45]

4.1.4 Electrochemical quartz crystal microbalance (EQCM)

EQCM (electrochemical quartz crystal microbalance) exploits the decrease of vibration caused by material deposited on the crystal surface, for example corrosion products. EQCM consists of a piezoelectric quartz oscillating at its resonant frequency, the frequency changes of which are dependent on the amount of deposited material. Usually, frequency changes decrease when material is adsorbed. EQCM is very sensitive to material and thickness changes. Earlier versions of these systems were extremely sensitive to temperature changes of the water, while more recent devices have addressed this problem successfully. Sensibility of QCM to pressure changes can prevent its widespread use in monitoring sensors. [46]

4.1.5 Zero-resistance ammeter (ZRA)

The galvanic couple technique (commonly known as the ZRA method) is a probe method to monitor galvanic corrosion and MIC. This technique is simple and can be used directly in systems operating at high pressure. The two electrodes used in the technique may have one of the following three configurations: 1) dissimilar metals or alloys (in which one is preferably more cathodic and another is preferably more anodic in the galvanic series), 2) same metal or alloy with a different metallurgical or electrochemical state, and 3) same metal or alloy of identical size and shape. In all configurations the electrodes are connected externally through a ZRA which measures the current between the couples. ZRA is quantitative when only one parameter affects the galvanic current, but in most field operating conditions more than one parameter affects the galvanic current. For these reasons this technique is only used as a qualitative indicator. [34]

4.1.1 Electrochemical noise (EN)

Noise is the general term used to describe the fluctuating behaviour of a physical variable with time. With respect to corrosion there are two types of noise: fluctuation in the corrosion potential (potential noise) and fluctuation in the current (current noise). Electrochemical noise EN is a probe method for early detection of general and localized corrosion. EN analysis of the potential and current noise pattern can indicate whether localized or uniform corrosion is occurring. However, EN requires expertise for the interpretation of the data obtained. The EN does not provide the quantitative rate for localized corrosion. [1,34,44]

4.1.2 Field signature method/ electrical field mapping (FSM/EFM)

The field signature monitoring (also known as EFM electrical field mapping) technique was developed originally to monitor internal corrosion of pipes and pipelines. It is a structural monitoring technique to determine general wall loss including that due to general corrosion, erosion, and localized corrosion. The measurement is made on the external surface of the structure rather than by inserting a probe into it. The idea of FSM is that several sensing pins are attached at various distances at the tested surface, and a current is applied into the tested surface through these sensing pins. The electric field pattern is detected by measuring the small potential differences among the pairs of sensing pins on the external surface. The electric field pattern depends on the geometry of the tested surface and general or localized corrosion on the internal surface produces changes in the electric field pattern. By comparing measured potential differences with baseline values for a similar uncorroded sample, the distribution and dimensions of corrosion on the internal surface can be computed. [1,34]

4.2 Specified monitoring methods for different types of localized corrosion

As a comparison to the common methods for localized corrosion monitoring in the next chapters the applied pitting, crevice, under-deposit and challenging environment corrosion monitoring types are separately discussed.

4.2.1 Pitting corrosion monitoring

Pitting corrosion is characterized by the presence of a number of small pits on the exposed metal surface. The geometries of the pits depend on many factors such as the metal composition and the surface orientation. The cyclic potentiodynamic polarization (CP) method is commonly used to qualitatively understand the pitting corrosion tendency of metals and alloys (see Chapter 4.1.3.). Another method to study pitting corrosion is the Cyclic galvano-staircase polarization (CGSP) method, which is used to determine the protection potential E_{prot}. The E_{prot} can also be determined according to the CP. The E_{prot} may be used as an indication of the susceptibility of a metal to localized corrosion. This method provides a quick method for determining the susceptibility to pit initiation, but it does not provide information about pit propagation. [34,47]

In a study by El Haleem et al. [48] the pitting corrosion current (corrosion rate) of reinforcing steel was measured under natural corrosion conditions in $Ca(OH)_2$ solutions in presence of Cl^- as aggressive ions and CrO^{2-}_4, HPO^{2-}_4, NO^-_2, WO^{2-}_4, and MoO^{2-}_4 as inhibiting anions. Performance of steel in this medium was determined by measuring corrosion current using a simple H -divided electrolytic cell. The study revealed that the corrosion current started to flow after the induction period which depends on solution composition (concentration, pH and presence or absence of the aggressive and the inhibiting anions). The limiting corrosion currents increased with increasing the Cl- ion concentration and decreased with increasing the pH and inhibiting ions concentration. The inhibition efficiency of the studied inhibiting ions increased in the following order: $CrO^{2-}_4 < HPO^{2-}_4 < NO^-_2 < WO^{2-}_4 < MoO^{2-}_4$, and depended on the way by which the inhibitor is added to the solution. Injection of the inhibiting anions in solution caused repassivation of the pre-formed pits through competition with Cl^- ions for adsorption sites on metal oxide surface. [48]

4.2.2 Crevice corrosion monitoring

In practice, crevices can be formed naturally (e.g. by biofouling, sediment, debris, and deposits) or man-made (e.g. by improper manufacturing, fabrication, or assembly). Crevice corrosion occurs in interstitial sites where a passive metallic material is locally in contact with a corrosive environment, whereas the majority of the metallic surface remains in contact with bulk liquid. Crevice corrosion results from local modifications of the solution within the confined area, which starts with local oxygen depletion. The susceptibility of a metal to crevice corrosion can be evaluated in the laboratory using ‘crevice formers’. These can be metal coupons, gasket washers, spacers, non-metallic strips, O-rings, and plateau assemblies. The occurrence of crevice corrosion is generally monitored by potential measurements, while the corrosion rate is difficult to detect, unless the creviced anodes and the surfaces sustaining the cathodic reactions are electrically separated and the current between them measured. [34]

Acoustic emission (AE) technique, based on the rapid release of energy within a material generating elastic wave propagation, was demonstrated to be a very powerful and sensitive technique to monitor and study microscopic mechanisms of localized corrosion such as stress corrosion cracking, abrasion or erosion corrosion, and pitting corrosion. In a study by Kim et al. [49] an attempt was made to monitor also crevice corrosion with AE. The aim of the work by Kim et al. [49] is to validate the use of AE for monitoring crevice corrosion on 304L austenitic stainless steel by controlling initiation, propagation and repassivation of crevice damage, and to find out the discriminating acoustic parameters. Corrosion potential and AE activity recording as well as visual observations of the development of crevice corrosion were in good agreement, which confirms the ability of AE technique for monitoring crevice corrosion. Crevice corrosion propagation leads to an increase of AE activity and to the emission of signals with high value of rise time, duration, counts number and cumulative energy. Acoustic parameters recorded have great similarities with those recorded during propagation of pitting corrosion on austenitic stainless steel. This suggests that the mechanism responsible for AE is quite the same, e.g. the evolution of hydrogen bubbles resulting from corrosion products hydrolysis and acidification within occluded pits, together with the friction of the bubbles along the walls and the cap covering the pits. [34,49]

In a study by Richter et al. [50] four different methods were used to analyze crevice corrosion: linear polarization resistance (LPR), harmonic analysis (HA), electrochemical noise (EN) and zero resistance ammetry (ZRA). Also a crevice corrosion probe LOCORR was applied (Fig. 9). The design of the probe imitates the conditions found in a crevice or under a deposit. In the probe a steel anode is covered by porous glass and the galvanic current between the anode and the steel casing of the cell is measured by ZRA. The results indicate that the probability of localized corrosion is low when the dissolved oxygen level is below 100 ppb. However the lifetime of the probe was relatively low due to high dissolved oxygen levels. The galvanic current measurements proved rather difficult to interpret since they were both dependent on the concentration of dissolved oxygen and the concentration of hydrogen sulphide. The EN measurements indicated that localized corrosion was taking place, though general corrosion was predominant. Both LOCORR and the EN measurements gave according to the authors promising results and have potential to be used in geothermal district heating systems, though the short life-time of the probe needs further studies. [50]

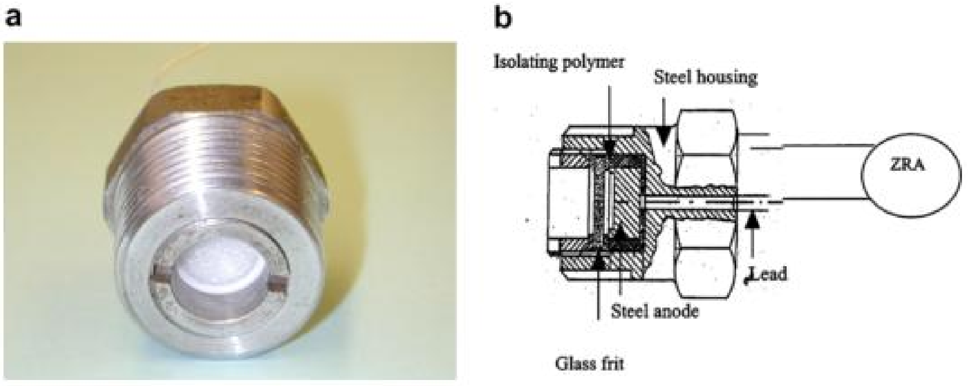


Figure 9. (a) Picture of the LOCORR cell, (b) schematic diagram of the LOCORR cell.

In a study by Lee et al. [51] a simple crevice corrosion monitor (a GAMRY potentiostat which was used as ZRA) was developed for mild and stainless steels. Monitor measures the electron coupling current, accurately followed the evolution of crevice activity, which results from cathodic process occurring on the external surface and partial anodic process developing within the crevice (the accumulation of H^+ and Cl^-). According to the authors the coupling current increases with time, and after initiation passes through a maximum, it starts to decrease, eventually changing sign to mark crevice inversion by gradual build-up of H^+. Monitor was used to follow the development of crevice corrosion in mild steel 1018, type 304 and type 410 stainless steels in sodium chloride solutions with and without corrosion inhibitor (anodamine). The monitor was able to measure the crevice initiation period, detect the crevice inversion, and determine inhibitor efficiency in reducing crevice activity. The monitor could accurately follow the evolution of crevice activity in terms of the cathodic process that occurs on the external surface (oxygen reduction) and that develops within the crevice due to the accumulation of H^+. [51]

4.2.3 Under deposit and challenging environment corrosion monitoring

Solid deposits on metal surface can cause a localized form of corrosion called under-deposit corrosion (UDC). UDC is often observed in cooling water systems where scales and foulants exist, and in oil and gas pipelines where sand, debris, biofilm and carbonate deposit are present. Methods to prevent UDC in industry include for example regular cleaning operations or corrosion inhibitor treatment. However, frequent cleaning treatment is troublesome, expensive, and not suitable for some pipeline systems. Also the effects of inhibitors on UDC are hard to prove since UDC is considered difficult to measure by normal corrosion testing techniques. Factors affecting UDC are retention of aggressive species in the deposits, failure of inhibitors to penetrate the deposits, a large cathode to anode surface area ratio and the possible formation of a localized differential concentration cell. It is considered that the accumulation of deposits on metal surface prevents corrosion inhibitors and biocides from accessing metal surface, leading to insufficient inhibitor concentration and accelerating anaerobic growth underneath deposits. This would mean that a higher concentration of inhibitor has to be used to prevent UDC than that would be needed to inhibit general corrosion. UDC often occurs in challenging environment of highly-resistive and inhomogeneous media. [43,45]

It has been studied by Tan et al. [45] that the combined electrochemical noise analysis (EN) and wire beam electrode (WBE, Chapter 3.1.7) method could have potential in measuring localized corrosion rates also for UDC. The WBE/EN -system has been utilised in experiments to measure electrochemical corrosion in challenging corrosion conditions such as multi-phase oil and gas mixtures, sand, a thin layer of electrolyte, under thermal insulation and under-deposit. In all these experiments, there was no need to apply an externally imposed polarization and no need of a counter electrode, and thus such problems were avoided as non-uniform polarization currents and IR drops associated with conventional polarization measurement. UDC processes were monitored in the experiments by mapping galvanic currents across the WBE to see how localized corrosion initiated and propagated under deposits and how it changed with the introduction of inhibitor (imidazoline) or oxygen (O_2). It was found that no under-deposit corrosion occurred in a CO_2 saturated pure brine solution under ambient temperature, however, when inhibitor imidazoline was introduced to the brine or when the environment was contaminated by O_2 under-deposit corrosion initiated. Increase in imidazoline concentration was found to reduce overall corrosion rates, but to enhance localized corrosion. The WBE system has also been proposed as a monitoring solution for challenging environments (see below). [43,45]

Corrosion processes in highly-resistive and inhomogeneous media can be very challenging to monitor due to complex mechanisms occurring during corrosion, which usually leads to various forms of localized corrosion. Also corrosion damages in challenging media are often hidden and concentrate on difficult-to-access areas that are buried, covered or wrapped by concrete, deposit or thermal insulation. The suitability of many traditional methods (for example ER, LPR, EIS) has been evaluated for monitoring corrosion of steel in various highly-resistive and inhomogeneous media such as steel specimen exposed to atmosphere and rebar buried in concrete structures. In many cases, these methods are also applied in combinations. However the traditional methods are inadequate in such challenging environment, where localized corrosion and difficult-to-access- areas are involved. One approach to tackle these practical difficulties is innovative design of miniaturised sensors/electrodes that can be embedded in, or emplaced on, various structures. Miniature sensors offer the possibility of overcoming practical difficulties associated with the installation and withdrawn of corrosion sensors in difficult- to-access areas such as configurational and structural overlaps. The miniature multi-sensor systems can be based on for example UT methods, LPR and EIS. However in principle miniaturised electrochemical sensors do not solve the IR potential drops and non-uniform polarization current distribution problems in highly resistive and inhomogeneous media.

Another approach is the development of novel electrochemical corrosion sensors that are able to avoid IR potential drops and non-uniform polarization current problems, and that are able to detect localized corrosion. Macrocell sensors, the so-called anode-ladder and expansion-ring, have been developed to monitor the corrosion risk of concrete structures. The anode ladder system consists of six single black steel anodes positioned 50 mm from the next one to prevent interactions between the anodes. The macrocell expansion-ring sensor consists of six measuring rings ('anodes') separated by sealing rings as parts of the main sensor and a 'cathode-bar', which are installed in small holes, to be drilled into the concrete structure. The basic measuring principle is to place several electrodes into a concrete structure at different depths and to measure the macrocell current, potentials and the electrical resistance of the concrete around the sensors. This sensor system detects the depth of the critical chloride content that may initiate depassivation and corrosion, and thus the time-to-corrosion can be estimated, enabling the owners of buildings to initiate preventive protection measures before cracks occur. In a typical experiment, it was found that the critical chloride content reached a depth of 5 mm into a concrete specimen about 80 days after concrete placement, which caused a significant increase of the macrocell current. However it was found that macrocell currents did not increase with chloride content and this result suggested that the sensor only gave an indication of galvanic activities due to the ingress of chlorides. The sensor did not give information on corrosion rates of steel in a concrete structure. [43,45]

5. Discussion and conclusions

The main idea when considering monitoring of scaling is to know the level of scaling and fouling in a system, and to be able to apply scaling removal methods in an efficient manner with the help of monitoring systems, which give feedback on the functionality of different cleaning methods. Different industries (for example paper mills, purified water systems and cooling water systems) have varying demands on the tolerable level of fouling and scaling depending of a given process. Also the development of biofilms and inorganic scale will differ greatly in different technical systems and process waters. [4]

The separation between organic and inorganic scale and fouling is possible, but how to apply this effectively in an on-line monitor, is yet a challenge. Also the fact, that organic and inorganic scales interact with each other, and may change the properties of each other, which will create further challenges. Use of fluorescent dyes together with the CLSM as mentioned in Chapter 3.3.2 can distinguish organic and inorganic scales, but it requires sample removal and staining of the removed samples to get the information. The use of fluorescent dyes in on-line applications seems at the moment unmanageable, since the staining of the scales in, for example, cooling water tubes and detecting them without sampling is very complicated. FTIR-ATR spectroscopy in a flow-through cell has a lot of potential for separation of different scales, but the detection of the scaling and fouling thickness remains unclear, since the maximum penetration depth of the IR beam in the medium is 1–2 µm. Perhaps another method could then be used beside for the thickness measurement. The BIOX and BIoGEORGE probes (Chapters 3.1.2 and 3.1.3) have been utilized commercially, but they do not provide information on nature of the deposits. It should be noted that some of the approaches mentioned in Chapter 3 have not exceeded above laboratory level, and therefore more investigation is needed. [4,11]

The use of multi-electrode array system (CMAS and WBE) for scaling and fouling monitoring as well as localized corrosion monitoring is much studied, and show good performance. Especially detecting deposits on metal surfaces and localized corrosion is manageable, but the ability to separate organic and inorganic deposits is not mentioned. The WBE can detect electrical resistances and potential differences on surfaces, so in theory, if the difference between organic and inorganic deposit resistance and/or potential is high enough, they could be distinguished. Of course, the corrosion currents will influence the results as well, and it could be that simultaneous detection off all features is too challenging. Therefore WBE method is proposed to be used in a combination with other systems, for example different scanning probes (Chapter 3.1.6). The traditional methods mentioned in the previous review [5] such as EIS and UT (or a combination of these), show also potential as a future monitoring method. For corrosion monitoring alone the EFM is interesting, since it does not require any probes to be inserted inside the tubes or structures. EFM is applied on the external surface, but receives corrosion data on the internal surface of the inspected structure. [1,30,34-36]

The optimal fouling and corrosion monitor should work without requiring sample removal, staining or other secondary procedures. The technique must function in an aqueous system and be specific for the monitored surface, i.e., minimize the signal from organisms or contaminants in the water phase. The monitoring systems should be based on correctly interpretable physical or electrochemical features to get reliable results. It appears that a development of a “tool box” with different monitoring devices could be the most potential solution for monitoring different properties and corrosion at the same time. [4]

6. Summary

Organic and inorganic deposit accumulation and related corrosion in different industry water systems create challenges, since they can cause damage or lower performance of the system, which results in efficiency losses. Many fouling prevention methods (chemical treatments etc.) are utilised in different water systems, but from the environmental and economic point of view alternative methods and/or more efficient use of the existing methods are needed.

To be able to apply the optimised level of biofouling and inorganic scaling prevention to different industry water systems, the monitoring of deposit accumulation is at key role. Detecting the type of deposits (organic and inorganic) is vital, and try-outs to tackle the separation have been made. Also detecting the localized corrosion related to scaling and fouling is important. Most methods are capable of detecting some properties (localized corrosion, deposit growth or different types of deposits) and function either off-line or on-line, but a method that could detect all at once, is not yet found. Therefore a monitoring system that is a combination of different methods could be potential. Different method combinations exist already (electrochemical impedance spectroscopy with ultrasonic technique, wire beam electrode method with sensing probes) and their suitability should be further studied.

References

[1] R. Cottis, Shreir's Corrosion, Chapter 4.36 Corrosion Monitoring and Inspection. 2010, pp. 3117–3166.

[2] M. Winters, "Simultaneous corrosion and fouling monitoring under heat transfer in cooling water systems," *Electrochemical Noise Measurement for Corrosion Applications*, pp. 230–246, 1996.

[3] Y. Cho, C. Fan, and B. Choi, "Theory of electronic anti-fouling technology to control precipitation fouling in heat exchangers," *International communications in Heat and Mass Transfer*, 1997.

[4] H. Flemming, "Role and levels of real-time monitoring for successful anti-fouling strategies-an overview," *Water Science & Technology*, pp. 1–8, 2003.

[5] M. Vepsäläinen and L. Carpen, "Biofouling and scaling mechanisms and monitoring techniques," VTT, 2012.

[6] D. Rubio, C. López-Galindo, J. F. Casanueva, and E. Nebot, "Monitoring and assessment of an industrial antifouling treatment. Seasonal effects and influence of water velocity in an open once-through seawater cooling system," *Applied Thermal Engineering*, vol. 67, no. 1–2, pp. 378–387, Jun. 2014.

[7] I. Janghorban Esfahani, M. J. Kim, C. H. Yun, and C. K. Yoo, "Proposed new fouling monitoring indices for seawater reverse osmosis to determine the membrane cleaning interval," *Journal of Membrane Science*, vol. 442, pp. 83–96, Sep. 2013.

[8] D. a. Al-Otaibi, M. S. J. Hashmi, and B. S. Yilbas, "Fouling resistance of brackish water: Comparision of fouling characteristics of coated carbon steel and titanium tubes," *Experimental Thermal and Fluid Science*, vol. 55, pp. 158–165, May 2014.

[9] K. O'Brien and I. Vuorinen, "Biofouling in Finnish powerplants by the hydrozoan Cordylophora caspia." Archipelago Research Instititute,Turku University, 2008.

[10] J. Kang, T. Kim, Y. Tak, J.-H. Lee, and J. Yoon, "Cyclic voltammetry for monitoring bacterial attachment and biofilm formation," *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 2, pp. 800–807, Mar. 2012.

[11] J. Linkhorst and W. J. T. Lewis, "Workshop on membrane fouling and monitoring: a summary," *Desalination and Water Treatment*, vol. 51, no. 31–33, pp. 6401–6406, Sep. 2013.

[12] L. Tian, X. D. Chen, Q. P. Yang, J. C. Chen, Q. Li, and L. Shi, "Effect of silica dioxide particles on the evolution of biofouling by Bacillus subtilis in plate heat exchangers relevant to a heat pump system used with treated sewage," *Chemical Engineering Journal*, vol. 188, pp. 47–56, Apr. 2012.

[13] W. F. Gale and T. C. Totemeier, Smithells Metals Reference Book (8th Edition). Elsevier, 2004.

[14] J. Morgan, Cathodic Protection (2nd Edition). NACE International, 1987.

[15] D. A. Bell, Electric circuits. Oxford University Press, 2009.

[16] R. Lambourne and T. Strivens, Paint and Surface Coatings - Theory and Practice (2nd Edition). Woodhead Publishing, 1999.

[17] The United States Pharmacopeial Convention, Food Chemicals Codex (9th Edition). The United States Pharmacopeial Convention, 2014.

[18] Springer, “Springer Materials, The Landolt-Börnstein Database,” 2014.

[19] American Chemical Society, “SciFinder,” 2014.

[20] G. Pavanello, M. Faimali, M. Pittore, A. Mollica, A. Mollica, and A. Mollica, “Exploiting a new electrochemical sensor for biofilm monitoring and water treatment optimization.,” *Water research*, vol. 45, no. 4, pp. 1651–8, Feb. 2011.

[21] M. Faimali, E. Chelossi, F. Garaventa, C. Corrà, G. Greco, and A. Mollica, “Evolution of oxygen reduction current and biofilm on stainless steels cathodically polarised in natural aerated seawater,” *Electrochimica Acta*, vol. 54, no. 1, pp. 148–153, Dec. 2008.

[22] M. Bruijs and L. Venhuis, “Biocide optimisation using an on-line biofilm monitor,” *Journal of Power Plant Chemistry*, vol. 31, no. 0, 2000.

[23] J. Klahre, “Monitoring of biofouling in papermill process waters,” *Water research*, vol. 34, no. 14, pp. 3657–3665, Oct. 2000.

[24] P. Cristiani, “Biofilm and MIC monitoring,” Brite-Euram III Themat. Netw. N° ERB BRRT-CT98-5084, 2000.

[25] ASPE Data Book - A Plumbing Engineer’s Guide to System Design and Specifications, Volume 2 - Plumbing Systems. American Society of Plumbing Engineers (ASPE), 2000.

[26] M. a. Winters, P. S. N. Stokes, P. O. Zuniga, and D. J. Schlottenmier, “Real-time performance monitoring of fouling and under-deposit corrosion in cooling water systems,” *Corrosion Science*, vol. 35, no. 5–8, pp. 1667–1675, Jan. 1993.

[27] A. B. Regberg, “The Effect of Dissimilatory Iron Reduction, Nitrate Reduction and Microbial Growth on Electrical Conductivity,” Dissertation in the Pennsylvania State University, 2011.

[28] A. Regberg, K. Singha, M. Tien, F. Picardal, Q. Zheng, J. Schieber, E. Roden, and S. L. Brantley, “Electrical conductivity as an indicator of iron reduction rates in abiotic and biotic systems,” *Water Resources Research*, vol. 47, no. 4, p. n/a–n/a, Apr. 2011.

[29] Y. Tan, “Sensing localized corrosion by means of electrochemical noise detection and analysis,” *Sensors Actuators B Chemical*, vol. 139, no. 2, pp. 688–698, Jun. 2009.

[30] Y. Tan, “An overview of techniques for characterizing inhomogeneities in organic surface films and underfilm localized corrosion,” *Progress in Organic Coatings*, vol. 76, no. 5, pp. 791–803, May 2013.

[31] W. R. Bowen, Hilal, and Nidal, Atomic Force Microscopy in Process Engineering - An Introduction to AFM for Improved Processes and Products. Elsevier, 2009.

[32] R. Oltra, V. Maurice, R. Akid, and P. Marcus, Local Probe Techniques for Corrosion Research (EFC 45). Woodhead Publishing, 2007.

[33] J. Davis, Engineering the Bioelectronic Interface - Applications to Analyte Biosensing and Protein Detection. Royal Society of Chemistry, 2009.

[34] S. Papavinasam, Corrosion Control in the Oil and Gas Industry. 2013.

[35] L. Yang and K. T. Chiang, "On-line and real-time corrosion monitoring techniques of metals and alloys in nuclear power plants and laboratories," Woodhead Publishing, vol. 14, pp. 417–455, 2010.

[36] A. Anderko, N. Sridhar, L. T. Yang, S. L. Grise, B. J. Saldanha, and M. H. Dorsey, "Validation of localized corrosion model using real time corrosion monitoring in a chemical plant," *Corrosion Engineering, Science and Technology*, vol. 40, no. 1, pp. 33–42, Mar. 2005.

[37] W. N. Al Nasser, F. H. Al-Salhi, M. J. Hounslow, and a. D. Salman, "Inline monitoring the effect of chemical inhibitor on the calcium carbonate precipitation and agglomeration," *Chemical Engineering Research and Design*, vol. 89, no. 5, pp. 500–511, May 2011.

[38] K.-L. Tung, H.-R. Damodar, R.-A. Damodar, T.-T. Wu, Y.-L. Li, N.-J. Lin, C.-J. Chuang, S.-J. You, and K.-J. Hwang, "Online monitoring of particle fouling in a submerged membrane filtration system using a photointerrupt sensor array," *Journal of Membrane Science*, vol. 407–408, pp. 58–70, Jul. 2012.

[39] W.-H. Chen, Y.-H. Hsieh, K. L. Tung, Y. L. Li, S. C. Lai, and N. J. Lin, "An Integrated Fouling Monitoring Technique for a Water Treatment Microfiltration Process," *Chemical Engineering & Technology*, vol. 33, no. 8, pp. 1269–1275, Jul. 2010.

[40] D. Spettmann and S. Eppmann, "Simultaneous visualisation of biofouling, organic and inorganic particle fouling on separation membranes," *Water Science & Technology*, 2007.

[41] G. Frankel and N. Sridhar, "Understanding localized corrosion," *Materials Today*, vol. 11, no. 10, pp. 38–44, 2008.

[42] D. R. Gunasegaram, M. S. Venkatraman, and I. S. Cole, "Towards multiscale modelling of localised corrosion," *International Materials Reviews*, vol. 59, no. 2, pp. 84–114, Jan. 2014.

[43] Y. Tan, "Experimental methods designed for measuring corrosion in highly resistive and inhomogeneous media," *Corrosion Science*, vol. 53, no. 4, pp. 1145–1155, Apr. 2011.

[44] L. R. Hilbert, "Monitoring corrosion rates and localised corrosion in low conductivity water," *Corrosion Science,* vol. 48, no. 12, pp. 3907–3923, Dec. 2006.

[45] Y. Tan, Y. Fwu, and K. Bhardwaj, "Electrochemical evaluation of under-deposit corrosion and its inhibition using the wire beam electrode method," *Corrosion Science*, vol. 53, no. 4, pp. 1254–1261, Apr. 2011.

[46] E. Wallhäußer, M. a. Hussein, and T. Becker, "Detection methods of fouling in heat exchangers in the food industry," *Food Control*, vol. 27, no. 1, pp. 1–10, Sep. 2012.

[47] S. Sharland, “A review of the theoretical modelling of crevice and pitting corrosion,” *Corrosion Science*, vol. 27, no. 3, pp. 289–323, 1987.

[48] S. M. Abd El Haleem, S. Abd El Wanees, E. E. Abd El Aal, and a. Diab, “Environmental factors affecting the corrosion behavior of reinforcing steel. IV. Variation in the pitting corrosion current in relation to the concentration of the aggressive and the inhibitive anions,” *Corrosion Science*, vol. 52, no. 5, pp. 1675–1683, May 2010.

[49] Y. Kim, M. Fregonese, H. Mazille, D. Féron, and G. Santarini, “Ability of acoustic emission technique for detection and monitoring of crevice corrosion on 304L austenitic stainless steel,” *NDT & E International*, vol. 36, no. 8, pp. 553–562, Dec. 2003.

[50] S. Richter, R. I. Thorarinsdottir, and F. Jonsdottir, “On-line corrosion monitoring in geothermal district heating systems. II. Localized corrosion,” *Corrosion Science*, vol. 49, no. 4, pp. 1907–1917, Apr. 2007.

[51] S. Lee, W. Kuang, and J. Mathews, “Monitoring Crevice Corrosion via the Coupling Current Part I: Detecting Crevice Activation, Inversion, and Inhibition,” *Power Plant Chemistry*, vol. 15, no. 4, pp. 240–250, 2013.