

MICROBially INFLUENCED CORROSION OF INDUSTRIAL MATERIALS

- BIOCORROSION NETWORK -

(Brite-Euram III Thematic Network N° ERB BRRT-CT98-5084)

Biocorrosion 00-01



MEETING OF TASK 5

held on April 13, 2000

at VENEZIA (Italy)

Istituto Grandi Masse (ISDGM-CNR)

Organised by P. CRISTIANI

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FOREWORD

Biofilm and MIC monitoring systems are still in their infancy in industrial plants, although they should be powerful tools to optimise biocide use, and consequently to protect environment against toxic effects and to save money.

One of the purposes of the Task 5 of the Brite-Euram thematic network "MIC of industrial materials" is to draw a complete state of the art of the biofilm and MIC monitoring systems, and then to try to estimate their performances with respect to the different application domains. The objective of this first Task 5 meeting was to achieve the first step of the state of the art by putting together the knowledge of the different partners of the network and of a few invited speakers.

The presentations that were done during the meeting proposed different approaches. R.Bott focused on IR and heat transfer devices, and evoked some physical techniques of biofilm mitigation. B.Tribollet presented an electrochemical monitor based on mass transfer measurements that are performed with natural (oxygen) or artificial (hexacyanoferrate) tracers. H.C.Flemming made an effort of classification of the numerous physical techniques, which are currently under development at the laboratory scale or in the field (optical fiber, differential turbidity measurement, quartz crystal microbalance, FTIR ATR-spectroscopy, friction resistance measurements...). He proposed to classify the devices into four levels, according to the type of information they are able to give. H.Jenner presented the practical approach and the field experience of Kema with impressive photographs of macro-fouling. He focused on the electrochemical BIOGEORGETM sensor, which was successfully applied on cooling water systems. A.Mollica showed the electrochemical principle of measurements to detect the early stage of biofilm growth in marine, river or fresh water systems and emphasised the simplicity of new devices, which have been successfully applied to optimise chlorination procedures in power plants. P.Cristiani presented the practical and financial benefits (up to hundred thousands Euro saved per year) resulting from the control of the chlorination procedure of a cooling system in ENEL's power plants using the new BIOX electrochemical system.

The approach presented by D.Féron did not specifically deal with biofilm monitoring, but with corrosion monitoring. He presented the practical experience of CEA on this topic. L.Hilbert focused on actual corrosion in sulphate media. She made a critical comparison of different techniques for corrosion monitoring (weight loss, electrical resistance, linear polarisation resistance, electrochemical impedance spectroscopy, electrochemical noise measurement, hydrogen permeation measurement...). Finally R.Wetgrove gave the view of chemical suppliers. He described the optical fouling control devices currently developed and used by Nalco.

The meeting was followed by the visit of Fusina power plant, in which BIOX system is operating to monitor some different, experimental, biocide treatments of the condensers cooling circuits. Fusina power plant belongs to the Italian ENEL Company; all the participants appreciated this opportunity, and they thank the staff of the plant for the very kind welcome.

The meeting was held at the *Istituto Grandi Masse, ISDGM–CNR*. We very much thank the Italian CNR for its hospitality. We also gratefully appreciated the help of Dr. V.Scotto, Dr. I.Trentin, and Dr. A.Mollica to organise the meeting, and of Dr. A.Bergel to edit these proceedings.

We would like to thank all the participants for their presentations and the enthusiastic discussions we had during the meeting.

Pierangela CRISTIANI
Centro Elettrotecnico Sperimentale Italiano
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LIST OF PRESENTATIONS

- GENERAL PRESENTATION
Pierangela CRISTIANI, Centro Elettrotecnico Sperimentale Italiano, Segrate, I
- BIOFILM MONITORING, PERSONAL EXPERIENCE
Reg BOTT, invited speaker, University of Birmingham, UK
- SENSOR FOR BIOFILM GROWTH
Bernard TRIBOLLET, invited speaker, CNRS, Université Pierre et Marie Curie, Paris, F
- MONITORING OF FOULING AND BIOFOULING IN TECHNICAL SYSTEMS
Hans Curt FLEMMING, IWW, Mülheim an der Ruhr, D
- BIOCIDES OPTIMISATION AGAINST BIOFILM BUILD-UP IN COOLING WATER SYSTEMS WITH THE BIOGEORGE™ SYSTEM
Henk A. JENNER, KEMA Power Generation, Et Arnhem, NL
- SIMPLE ELECTROCHEMICAL SENSORS FOR BIOFILM AND MIC MONITORING
Alfonso MOLLICA, Istituto per la Corrosione Marina dei Metalli, Genova, I
- IN-FIELD EXPERIENCE
Pierangela CRISTIANI, Centro Elettrotecnico Sperimentale Italiano, Segrate, I
- MIC MONITORING : CEA PRACTICE
Damien FERON, CEA - CEREM, Saclay, F
- MONITORING TECHNIQUES FOR MIC OF CARBON STEEL
Lisbeth HILBERT, The Technical University of Denmark, IPT, Lyngby, D
- OPTICAL FOULING MONITORS
R.L. WETEGROVE, invited speaker, Nalco, USA

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Development of Biofilm Monitoring at the School of Chemical Engineering, University of Birmingham, UK

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INTRODUCTION

Work at the School of Chemical Engineering at the University of Birmingham on the effects of operating variables on the development of biofouling in flowing systems, and the effectiveness of control methods, involving biocides and biocidespersants or physical techniques, requires the need to monitor the accumulation of biofilms on surfaces. The apparatus employed is a relatively large scale laboratory pilot plant, that simulates a cooling water system under carefully controlled conditions. The principal aim is to study biofilm accumulation on tubes that represent either heat exchanger tubes, or pipelines in a cooling system. Fig. 1 gives a schematic flow diagram of the equipment.

EARLY METHODS OF MEASUREMENT

Weighing

At the inception of the work some twenty years ago, the tubes (on which the biofilm grew) were removed from the system, drained carefully according to a standard procedure and then weighed. The difference between the mass of the fouled tube and its previous mass in the clean condition, give the accumulation of biofilm. Assuming that the density of water represents the density of the biofilm it was then possible to calculate the mean biofilm thickness knowing the tube dimensions. The principal difficulty was the test had to be interrupted with the potential for affecting the quality of the data obtained.

Conductivity measurement

Another early technique that was used with some success, was to use the electrical conductivity of the biofilm in conjunction with a micrometer. The arrangement is shown on Fig. 2. The micrometer is screwed down till the needle touches the biofilm, when a deflection on the ammeter is observed. The micrometer reading is noted. The needle is further screwed down till a second deflection is observed when the needle touches the metal surface on which the biofilm resides. The difference between the two readings is the thickness of the biofilm at the point of measurement. Fig. 3 shows a channel of square section that had removable plates for testing. Semi circular test plates have also been used.

The principal drawbacks to the method are that only a point measurement is given that is unlikely to be representative. A series of measurements was needed therefore, to give a more average value, but again due to the limits of the size of the test surface, this may not have been representative. As with the weighing method the test had to be interrupted for the measurement to be made. The removal of the test plate from the flow channel may also have damaged the biofilm thereby adding to the unreliability of the data. A further difficulty with the technique was ensuring that the test plate was flush with the internal surface to avoid irregularities with consequent effects on the flowing that would affect the biofilm growth. Attempts to carry out the measurement in situ were not successful.

CURRENT TECHNOLOGY

To make measurements in situ, without disturbing the flow conditions, is an essential requirement for reliable data to be obtained. Two technologies have been used.

Infra red absorbance

The monitor which has undergone considerable development over the past few years uses the absorbance of emitted infra red as a measure of biofilm accumulation. It requires a transparent tube on which the biofilm develops, through which the infra red radiation passes. Glass is of course, not a usual material of construction but its use can be justified on the grounds that the data obtained are suitable for comparison with other data obtained in the same way. It is possible to traverse the length of tube to obtain a number of point readings to provide an average thickness. Visual inspection is also possible. Thus the effects of variables can be determined and the effectiveness of different biocides or physical methods of biofilm control, can be demonstrated during continuous operation. Fig. 4 shows a typical "head" that fits around the glass tube. The technique is under continuous development to improve the reliability of data, using data logging equipment and continuous graph plotting, and is extensively used in current research. Fig. 5 shows data obtained at two different velocities. Fig. 6 shows the effect of biocide concentration at two different velocities. Fig. 7 presents data from a power station cooling water system. The excursions of absorbance are due to chlorine addition.

Measurement of heat transfer resistance

A monitor developed by the National Engineering Laboratory (NEL) in the U.K. determines the heat transfer resistance due to the presence of a biofilm; the heat transfer resistance is a measure of the biofilm accumulation. The monitor is particularly useful for testing fouling propensity in the field using a side stream from the plant under surveillance; but it is also useful for laboratory pilot plant studies. A schematic diagram of the monitor is given in Fig. 8. By making a heat balance across the monitor in conjunction with temperature measurements it is possible to "back off, the thermal resistance of the biofilm. The calculation can be carried out automatically by computer so that a continuous record of the change in the accumulation of biofilm can be obtained.

In a particular laboratory test a series of four monitors was used in order to provide collaborative data. The test was needed since it was feared that a particular hot process water would cause biofouling problems in heat exchangers planned to be installed to recover heat. Fig. 9 is an example of the data obtained demonstrating that fouling was not likely to be a problem. The effect of temperatures in the range of 50-80°C and velocities from 1.0 to 1.6 m/s were studied. Heat exchangers were installed on this evidence that have operated for at least one year with no biofouling problems.

CONCLUDING REMARK

The experience is that the monitors currently used both in the laboratory and in the field are capable of providing data on which design may be based and control may be exercised.

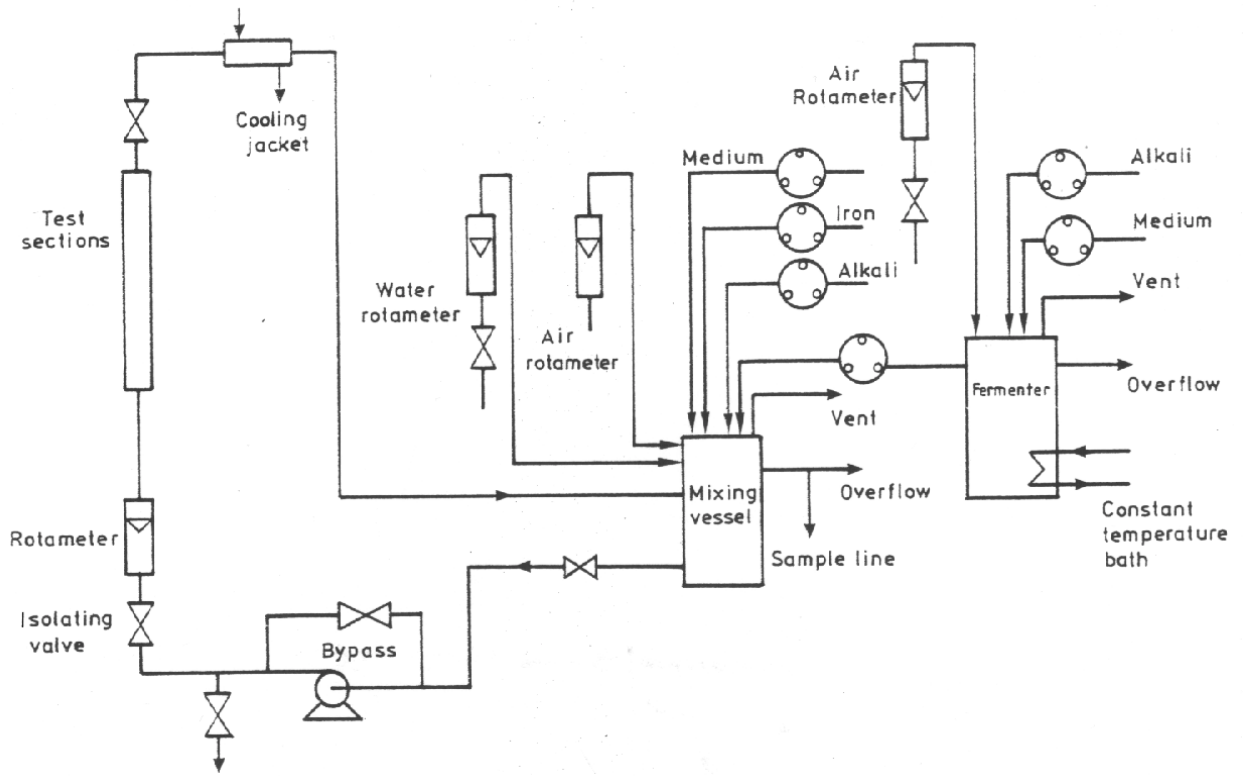


Fig. 1 - Flow diagram of laboratory pilot plant.

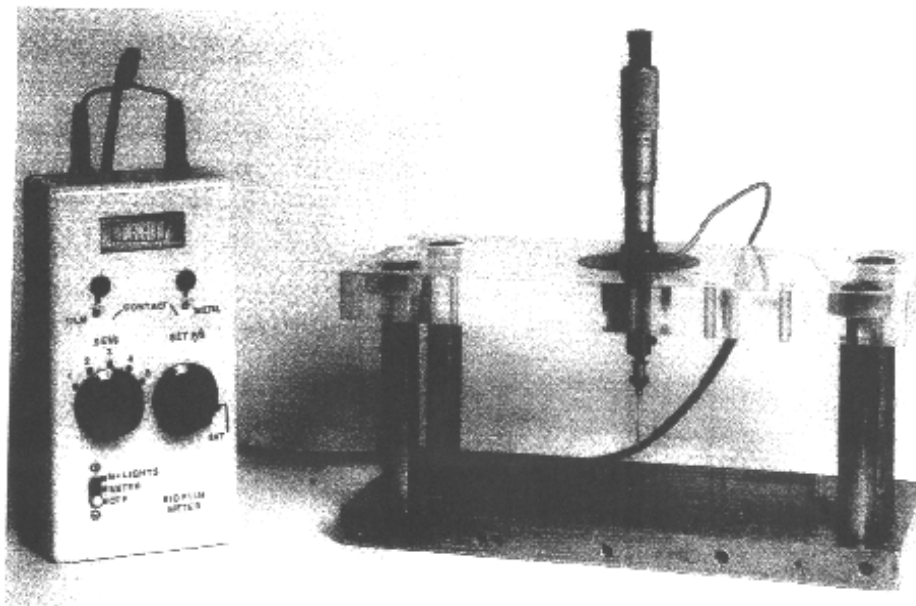


Fig. 2 - Electrical conductivity measuring device.

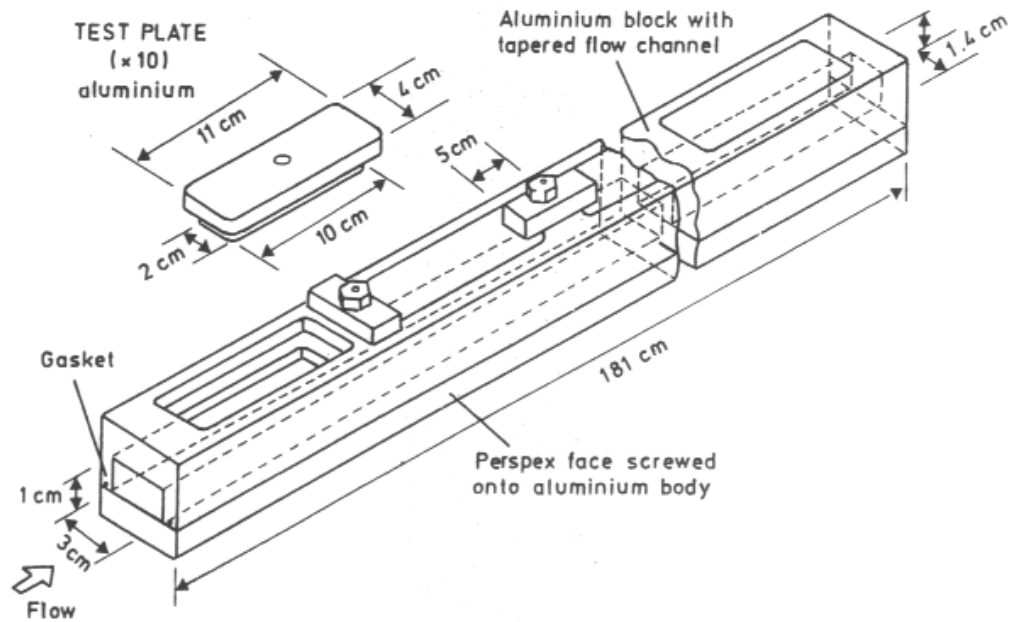


Fig. 3 – Square channel with removable plates

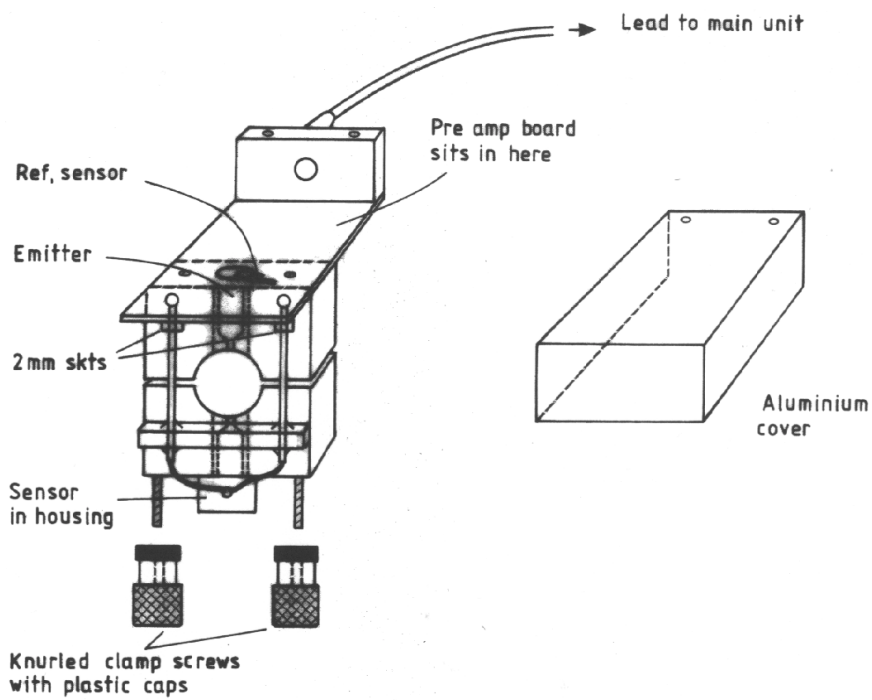


Fig. 4 – Infra red sensing monitor.

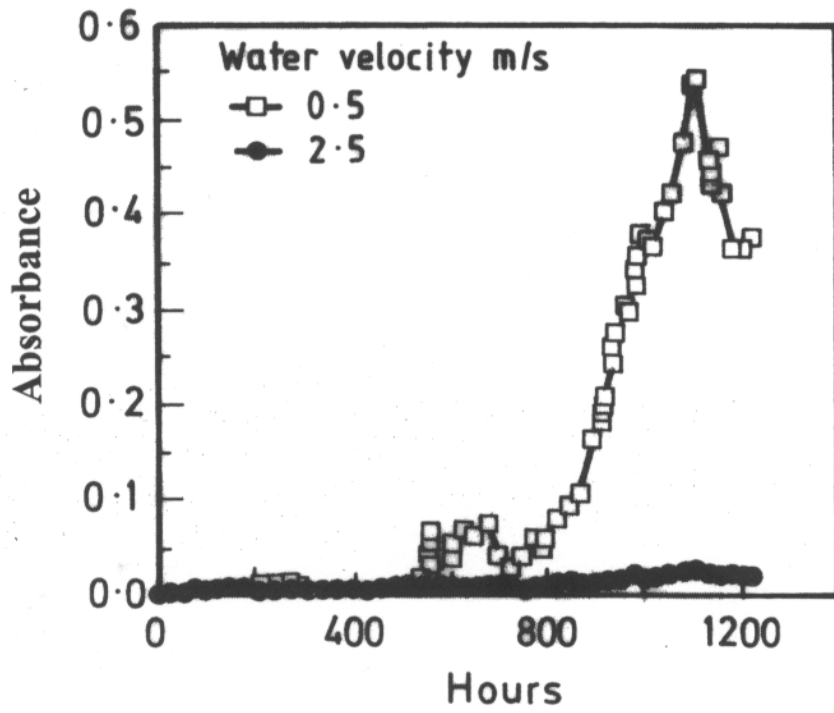


Fig. 5 - Absorbance due to biofilm development at two different velocities.

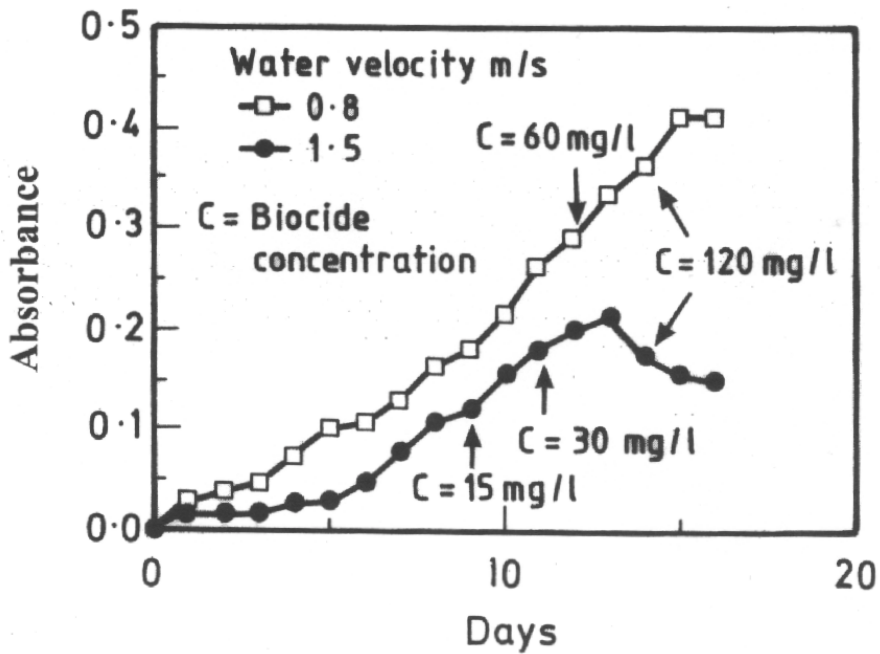


Fig. 6 - The effect of biocide concentration at two different velocities.

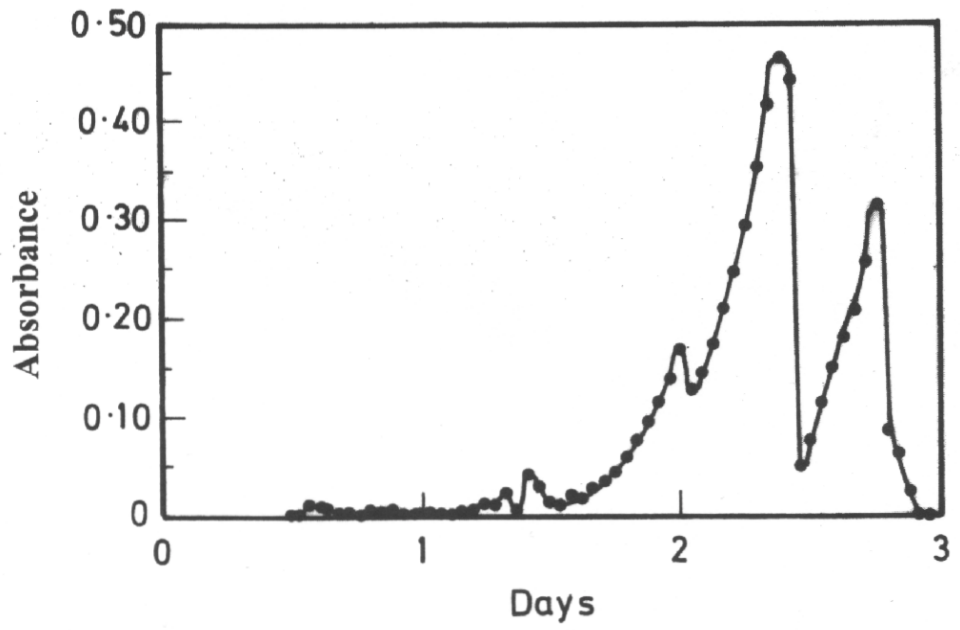


Fig. 7 – Absorbance monitor data for a power station cooling water system

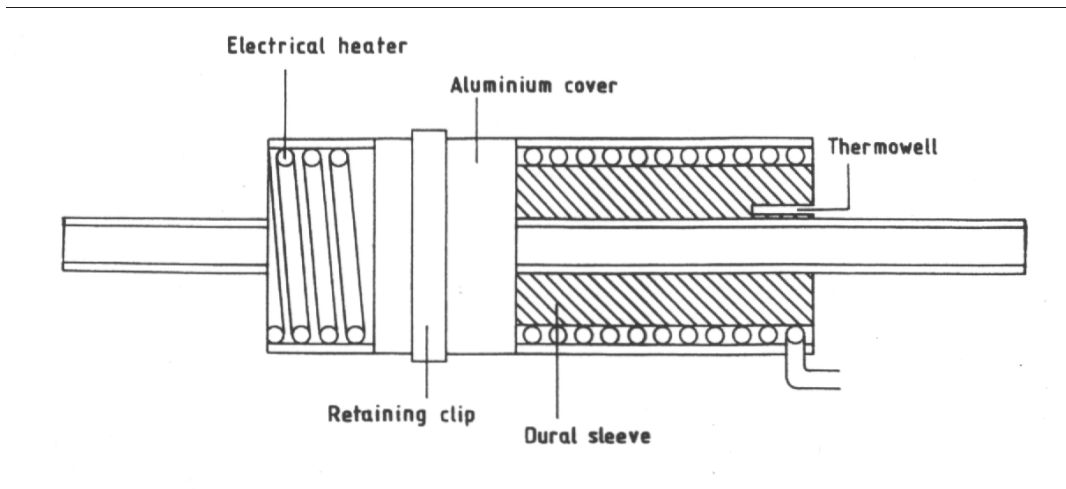


Fig. 8 – Basic design of NEL monitor

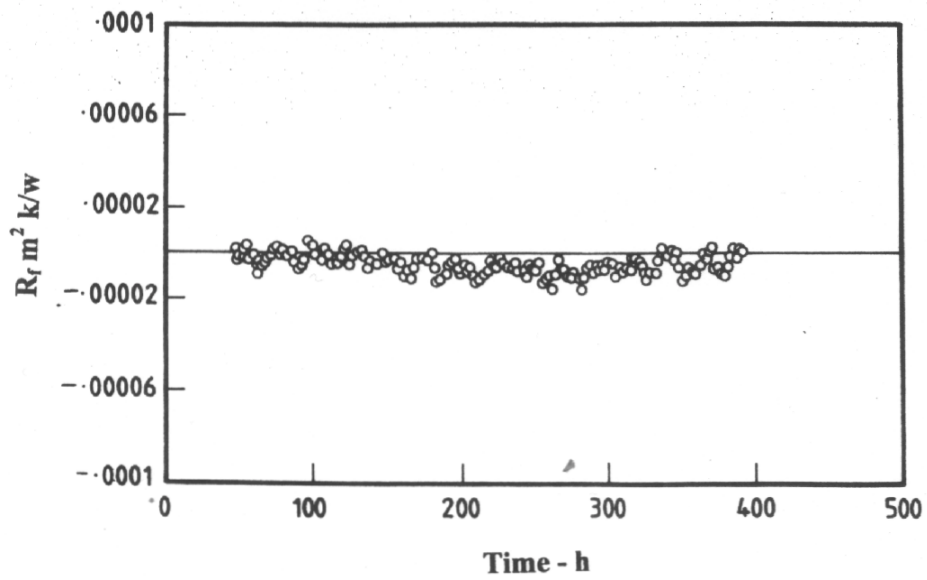


Fig. 9 – Heat transfer resistance data obtained with the NEL monitor.

SENSOR FOR BIOFILM GROWTH

Bernard TRIBOLLET

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Introduction:

Biofilms are generally composed of microbial cells and their products (extracellular polymers), which confer to them a very porous structure, in agreement with the amount of water contained (>95%) [1, 2]. The distribution of microorganisms is not uniform. In multi-species biofilms, highly complex structures containing voids, connecting channels between these voids, and microbial clusters or layers were predominantly found [3]. With respect to mass transport, biofilms behave as an inert porous layers. By EHD impedance analysis [4,5], it was shown that the diffusion coefficient in the biofilm D_f is the same as the diffusion coefficient in the electrolyte D . The porosity of the biofilm is, therefore, close to 1, in agreement with the amount of water contained.

Mass transport analysis through a porous layer:

When reacting species are oxidized or reduced in a fast reaction at a metallic electrode coated by a porous layer, their concentration gradient is distributed between the porous layer, where mass transport is controlled by molecular diffusion, and the electrolyte solution, where it is controlled by convective diffusion [6] (Fig. 1.).

At a given potential corresponding to the tracer diffusion plateau, a current density is measured as a function of the electrode rotation speed. The steady-state current can be analytically calculated as follows, according to the Levich theory [7] and Deslouis *et al.* [6]:

$$i = i_o + \frac{1}{i_f^{-1} + i_L^{-1}} \quad \text{with} \quad i_f = \frac{nFD_f c_\infty S}{\delta_f} \quad (1)$$

and where i_o is a non diffusional current, corresponding for example to the hydrogen reduction, D_f is the diffusion coefficient in the film, c_∞ the concentration of the electroactive species in the bulk solution, δ_f is the porous layer thickness, F is the Faraday constant ($F=96485$ Cb), n is the number of electrons ($n=1$ in the case of the ferricyanide and 4 for the oxygen), S is the active electrode area ($S=0.785$ cm²).

The porous layer consists of a biofilm developed on an inert gold electrode (10 mm diameter) during the immersion time in natural water. Two tracers were used ($\text{Fe}(\text{CN})_6^{3-}$ and oxygen) in seawater but in fresh water, only the ferricyanide tracer was used. The ferricyanide tracer was used when the solution of biofilm development is not very conductive, *e.g.*, for the case of the fresh water, its use prevented formation of calcium carbonate scale on the electrode. The $\text{Fe}(\text{CN})_6^{3-}$ diffusion coefficient is $5.6 \cdot 10^{-6}$ cm².s⁻¹ and the concentration is fixed at $2 \cdot 10^{-3}$ M. The oxygen tracer has the advantage of being naturally present in the medium. The oxygen diffusion coefficient is $1.6 \cdot 10^{-5}$ cm².s⁻¹, its concentration was about $2.2 \cdot 10^{-4}$ M, and was precisely determined by the polarographic method during the measurements.

With the two tracers (ferricyanide and oxygen), the polarization curves allow the kinetic evolution to be followed with the biofilm development on the electrode surface.

In Fig. 2., the polarization curves show an evolution with time in the ferricyanide plateau between 0 mV/SCE and -400 mV/SCE. When the time increases, the biofilm grows and the current density decreases.

Then with Eq.1, for the ferricyanide : $\delta_f = nFD_f c_\infty S(i(t)^{-1} - i_L^{-1})$ (2)

For the oxygen, i_0 is different of zero and may be determined just after the immersion:

$$\delta_f = nFD_f c_\infty \left((i(t) - i_0)^{-1} - (i(0) - i_0)^{-1} \right) \quad (3)$$

Sensor description [8,9]:

The flow used for the sensor is an impinging jet flow described in Fig 3. A picture of the overall sensor is given in Fig 4. The sensor is composed of six identical electrodes in front of six nozzles, the electrode diameter is corresponding to the stagnation region. The main flow, corresponding to the biofilm growth, is developed between the input valve and the output valve (Fig. 5). For the measurement itself, the two input and output valves are closed and the pump is working to generate the impinging flow for each electrode which is polarised at a potential corresponding to the limiting current for the electrochemical tracer under consideration. For each electrode the current is recorded versus the flow rate and by using equation (2) or (3) the corresponding biofilm thickness is determined.

As an example the average thickness obtained on the six electrodes is plotted versus the flow rate (Fig. 6). The elastic behavior of the biofilm appears on this result, the biofilm is thicker at low flow rate and becomes thinner for higher flow rate. It was shown [8], that this elastic behavior is depending of the water and on the hydrodynamic corresponding to the biofilm growth.

References:

1. WG. Characklis, *Biofilms*, (Edited by W. Characklis and KC. Marshall) J. Wiley and Sons, New York (1990).
2. PL. Bishop, TC. Zhang and YC. Fu, *Wat. Sci. Tech.*, **31**, 143 (1995).
3. HA. Videla, *Manual of Biocorrosion*, (Edited by CRC) Lewis Publishers, Florida (1996).
4. E. L'Hostis, C. Compère, D. Festy, B. Tribollet and C. Deslouis, *Corrosion*, **43**, 4 (1997).
5. E. L'Hostis, PhD thesis, University of Paris VI (1996).
6. C. Deslouis, B. Tribollet, M. Duprat and F. Moran, *J. Electrochem. Soc.*, **134**, 2496 (1987)
7. V. G. Levich, *Physicochemical Hydrodynamics*, Prentice Hall, Englewood Cliffs, New Jersey (1962).
8. D. Herbert-Guillou, Thèse de l'Université Pierre et Marie Curie, Paris (2000).
9. L. Kiéné, D. Festy, B. Tribollet, D. Herbert-Guillou, "Procédé et dispositif pour la détection d'un biofilm", Patent N° FR 00 00228 (january 10th 2000).

Figure 1: Mass transport through a porous layer

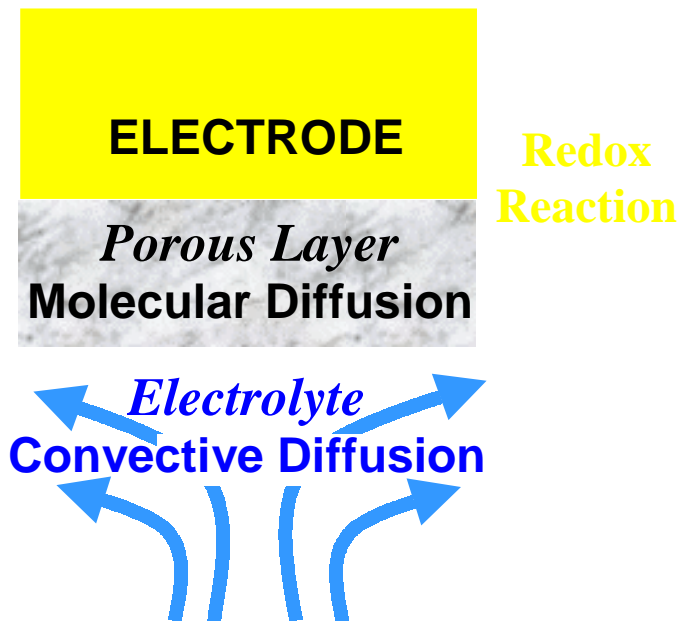
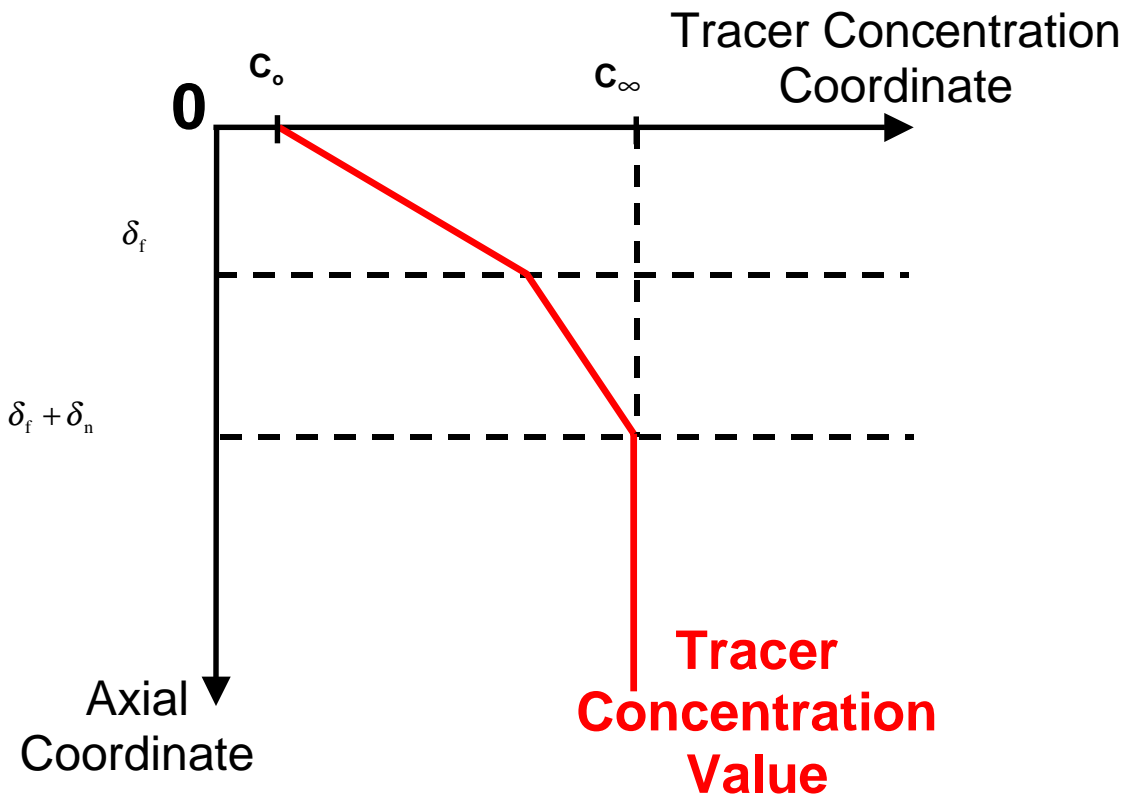


Figure 2: Current-potential curves plotted for different immersion time

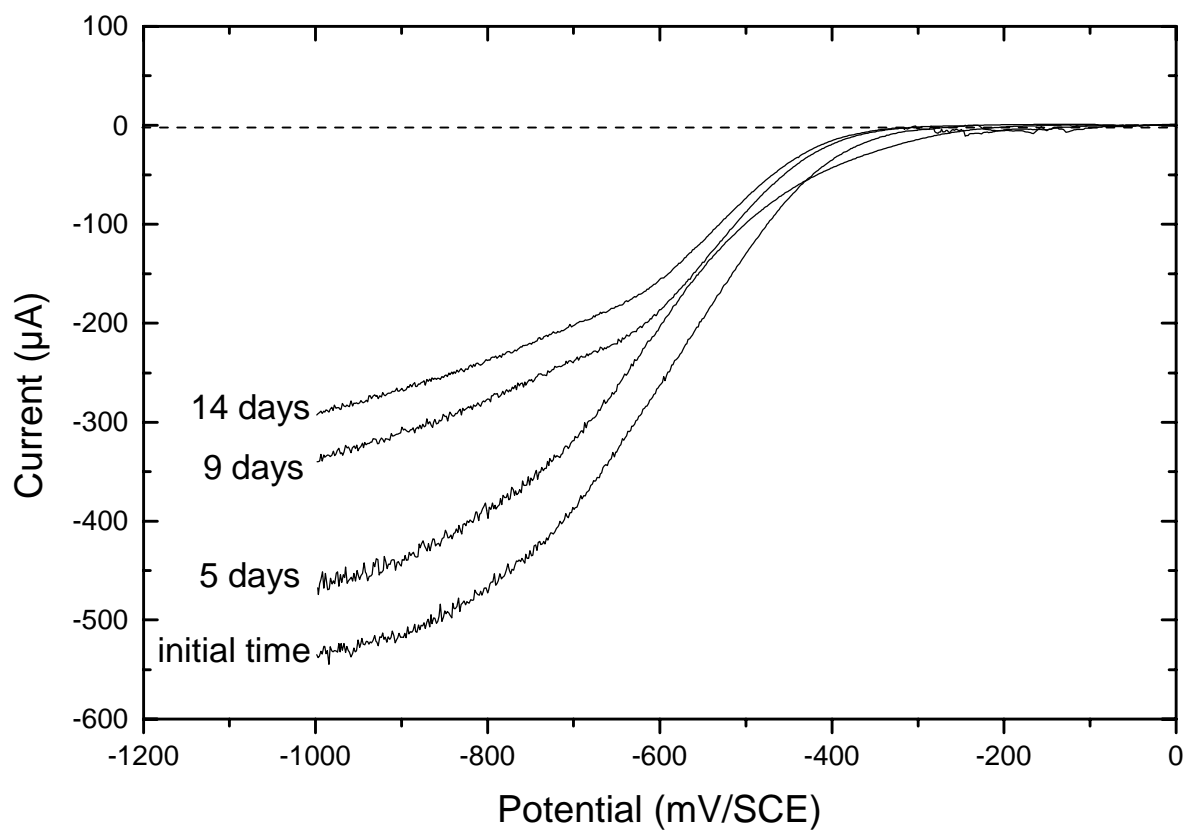


Figure 3: Impinging jet flow

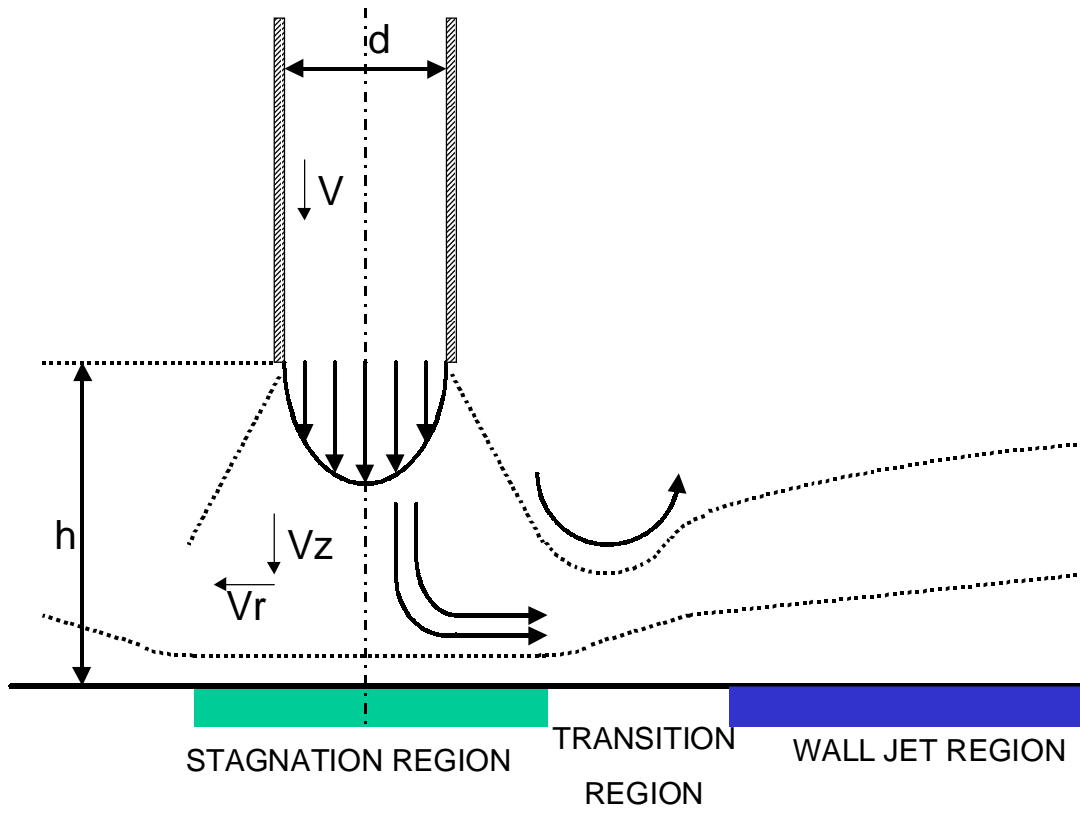


Figure 4:

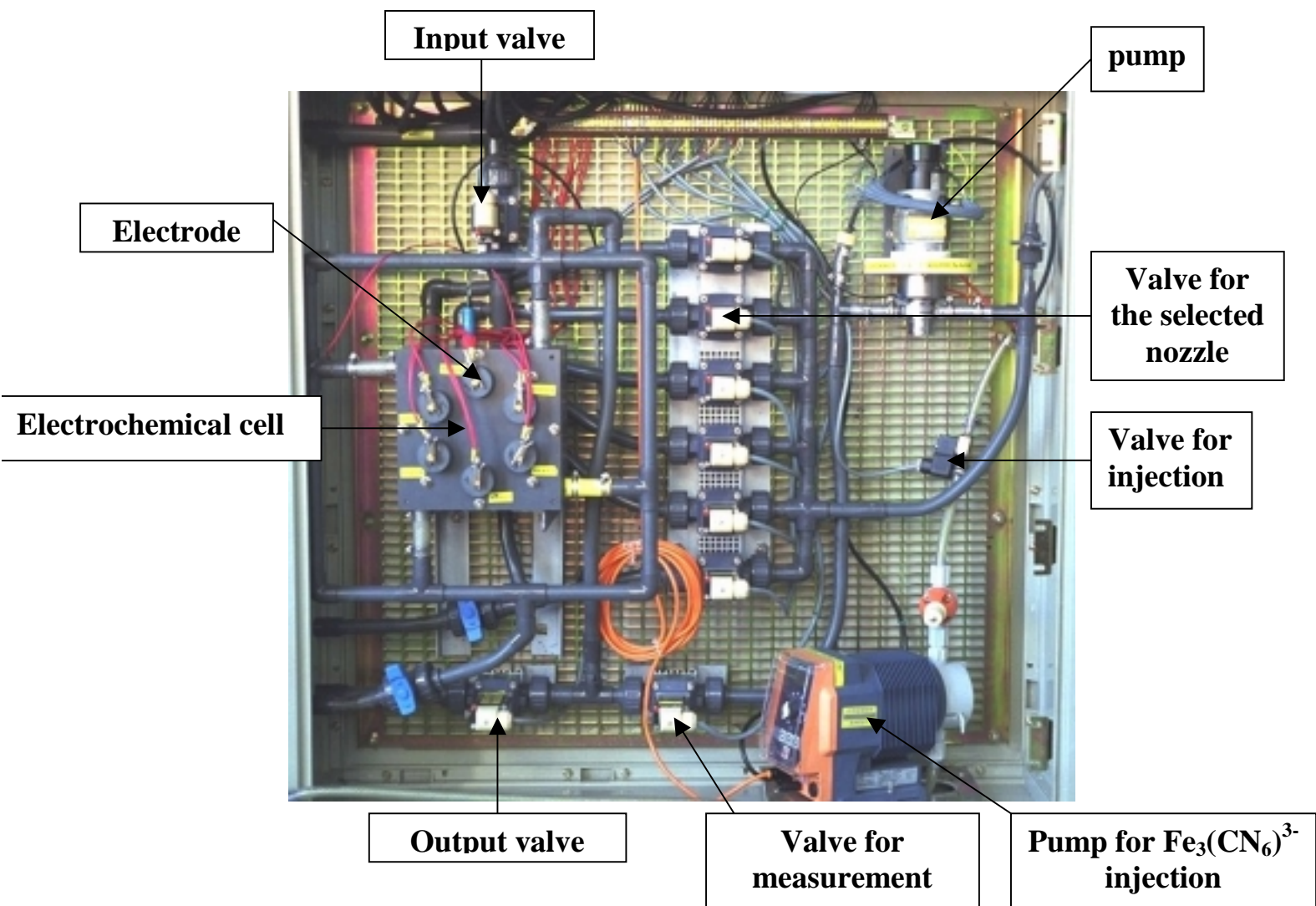


Figure 5:

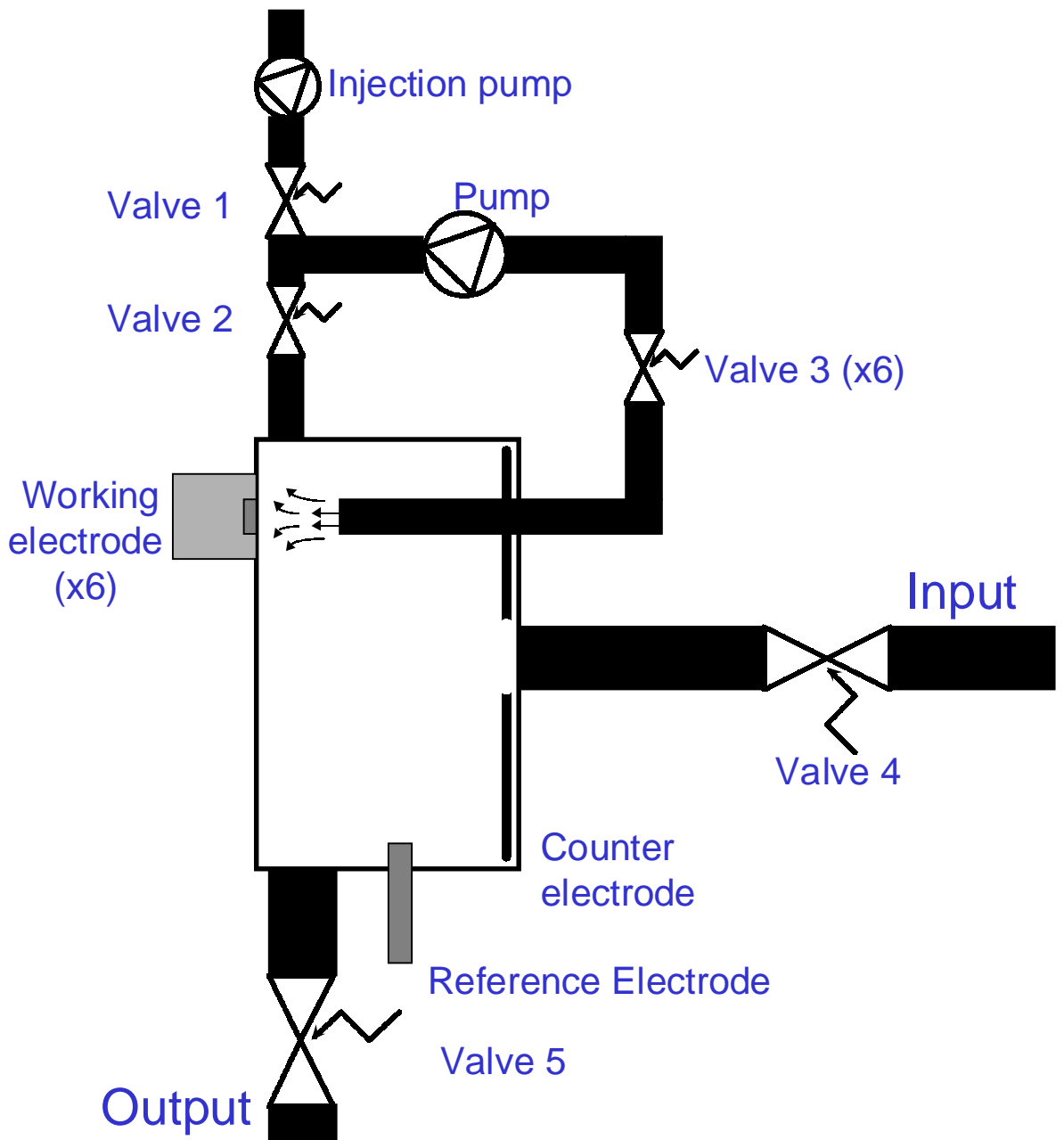
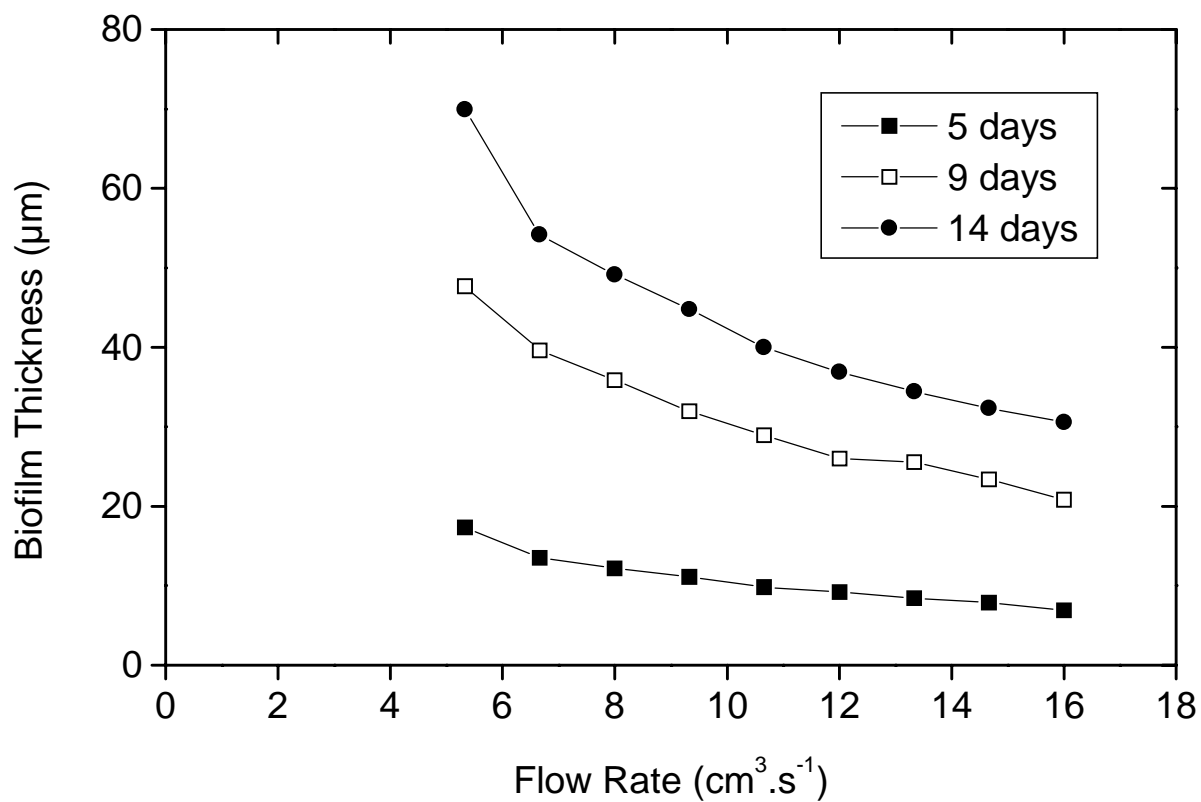


Figure 6: Variation of the biofilm thickness versus the flow rate



MONITORING OF FOULING AND BIOFOULING IN TECHNICAL SYSTEMS

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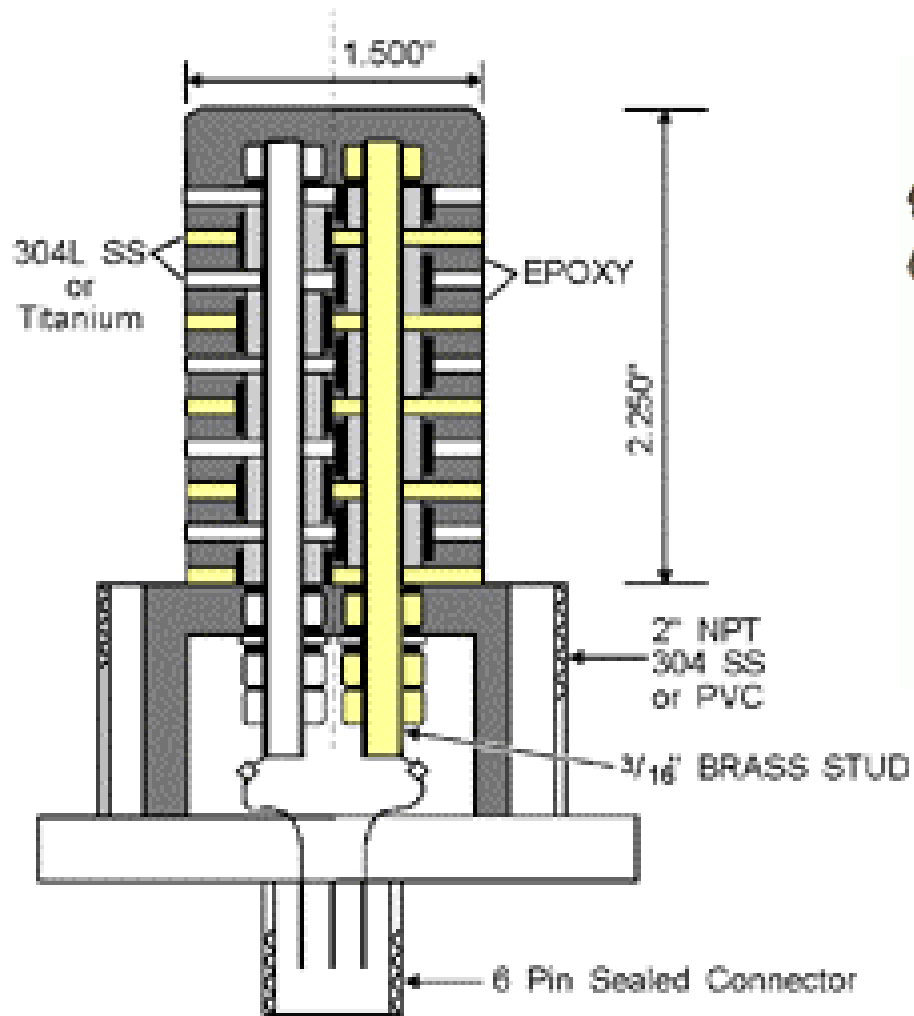
The main part of this presentation has been published in:

MONITORING OF FOULING AND BIOFOULING IN TECHNICAL SYSTEMS
Flemming H.C., Tamachkiarowa A., Klahre J., Schmitt J.,
Wat. Sci. Technol, 38, 1998, 291-298.



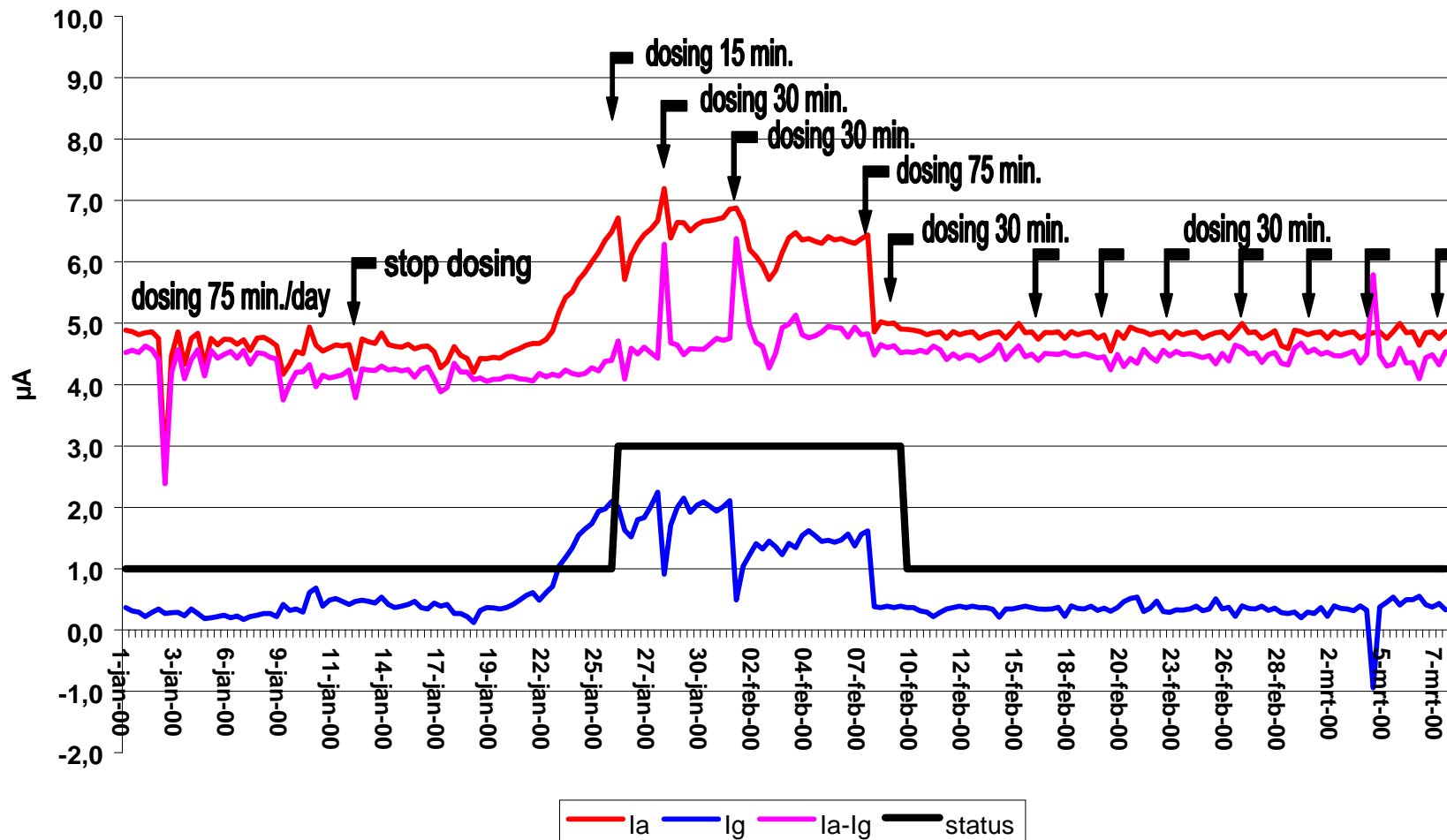
Biocide optimisation against biofilm build-up in cooling water systems with the BloGEORGE™ system

- **Principle BloGEORGE™ on-line monitoring system**
- **CASES**
 - **Once through CWS of a waste incinerator plant**
 - **Open recirculating CWS of a power plant**



Once-through CWS

- waste incinerator unit (63 MWe)
- cooling water flow per unit: 11.000 m³/h
- product: Na-hypochlorite
- regime: 75 min./day (0,60 mg/l TRO)
- installation **BloGEORGE™**: behind condenser in a blinded flange
- monitoring period: 18 Nov 1999 - 8 Mar 2000
- brackish water temperature: 15 - 20 °C



Conclusions

- dosing Na-hypochlorite 2x 30 min./week (0,60 mg/L TRO) is sufficient to prevent biofilm build-up at water temperatures $< 20^{\circ}\text{C}$
- achieved reduction (new regime) of Na-hypochlorite = 85%

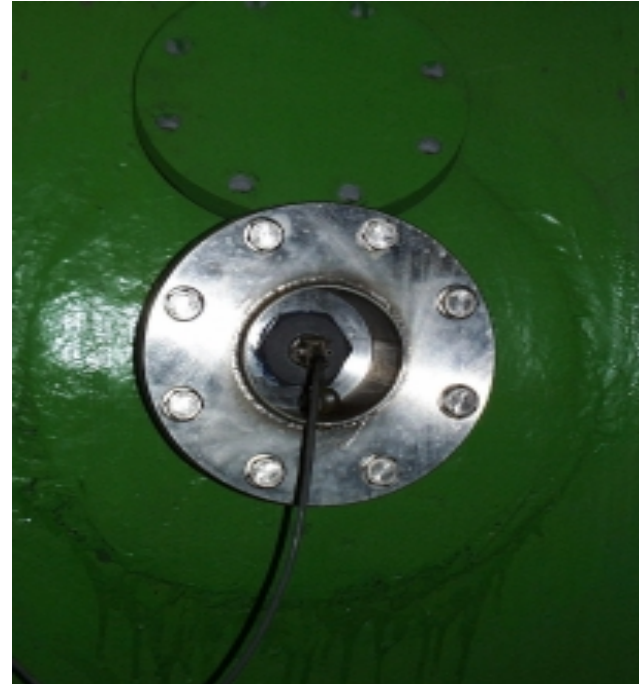
Open recirculation CWS with hybrid cooling tower (forced)

- **power plant (220 MWe)**
- **cooling water flow per unit: 12.960 m³/h**
- **product: ozone**
- **regime: 2x 2 hours/day (0,30 mg/L)**
- **installation BloGEORGE™: at inlet and basin tower**
- **monitoring period: 6 Jun 1999 - 9 Aug 2000**
- **fresh water temp: inlet 36,3°C - outfall 23,8°C (RH 60%, temp. 15°C)**

Conclusions

- **ozone is effective against biofilm build-up before and after heat exchangers up to the cooling tower**
- **biofilm build-up in cooling tower basin due to stripping ozone and nutrient input from the coolant air**
- **filling of the tower is reasonable clean**

- **SECOND PART : GDA waste incinerator**

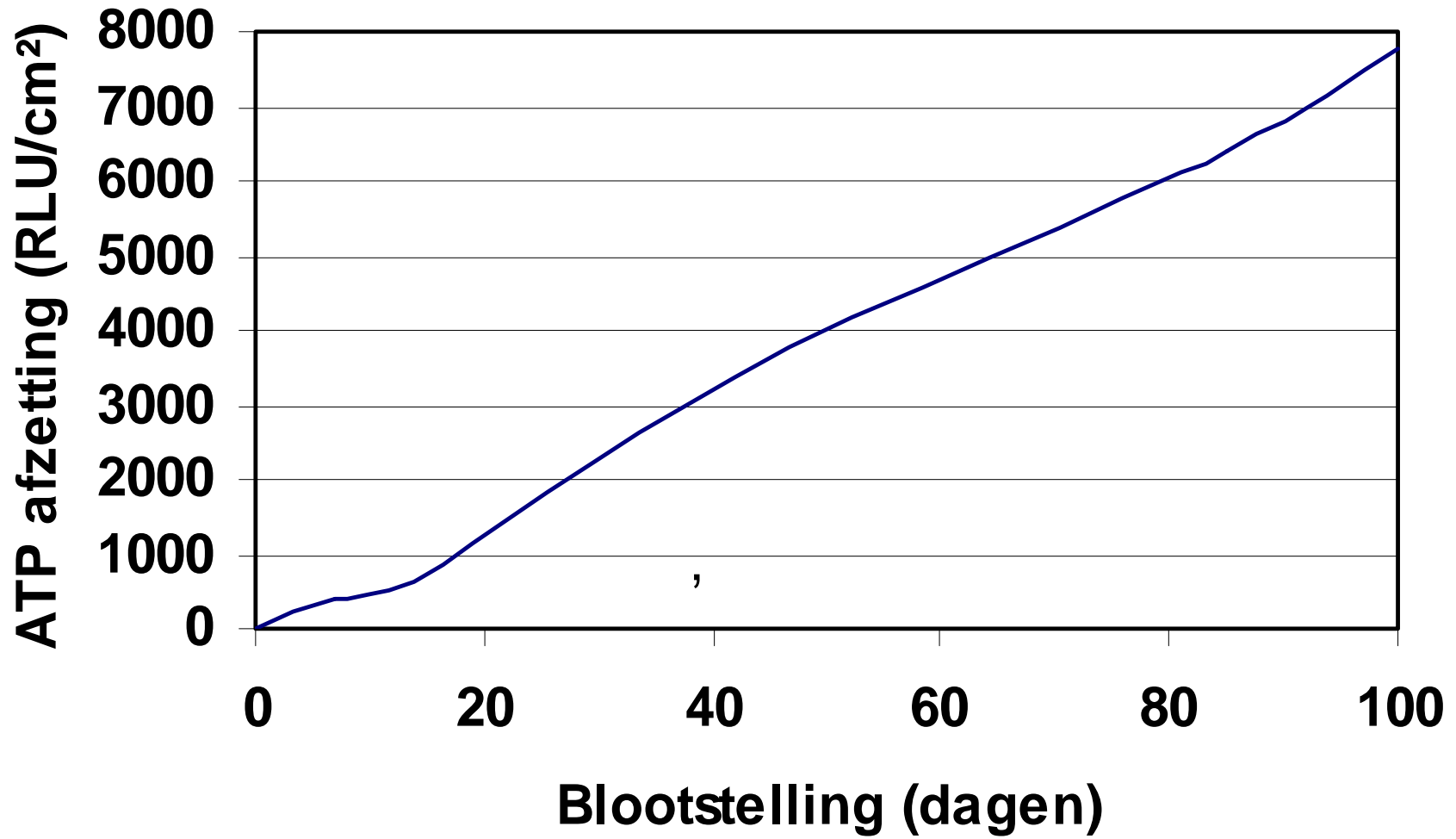


THIRD PART

power station Rotterdam







Simple electrochemical sensors for biofilm and MIC monitoring

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ICMM-CNR

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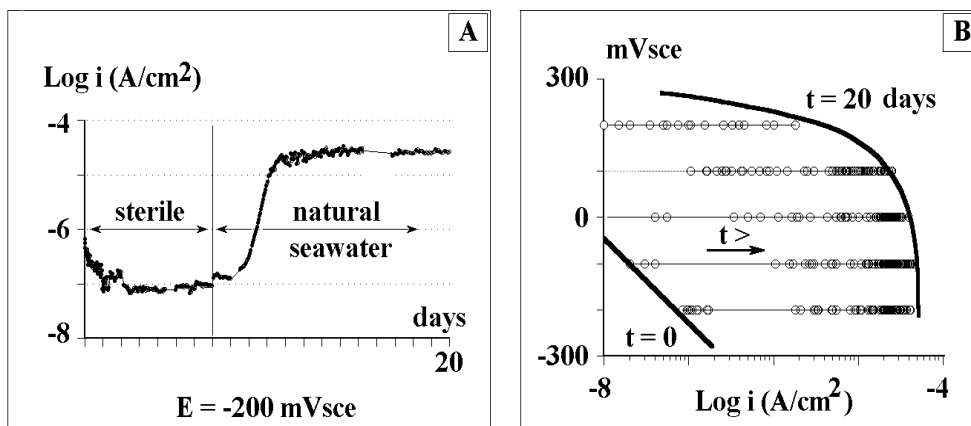


Fig 1 - The phenomenon of “cathodic depolarization” induced by biofilm growth on Stainless steel surfaces exposed in natural waters.

- A) An example of the trend of cathodic current measured on SS polarized at -200 mVsc and exposed first in sterile seawater and then in natural seawater. Biofilm formation on steel surfaces once exposed in natural seawater causes a sharp increase of the cathodic current.
- B) By repeating the previous test at different imposed potential the whole shift of the cathodic curve due to the biofilm formation on SS surfaces is obtained.

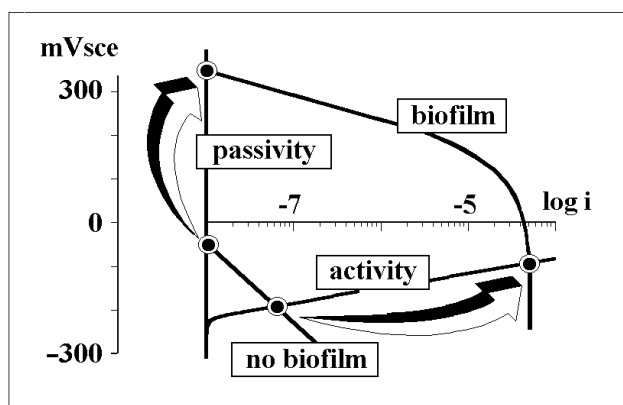


Fig 2 - The phenomenon of “cathodic depolarization” causes corrosion. The scheme shows that biofilm formation, through “cathodic depolarization”, induced by the biofilm growth causes :

- a sharp increase of the free corrosion potential of SS in passive state promoting, in so far, an higher probability of localized corrosion onset,
 - an higher propagation rate of localized corrosion in act (active state).
- Galvanic corrosion of less noble alloy coupled with SS are also increasing when biofilm forms on SS surfaces.

Fig 3

Based on the phenomenon of “cathodic depolarization”, very simple electrochemical devices for biofilm monitoring can be realized.

A SS electrode coupled, through an external cable, to a less noble alloy (iron anode as an example) can be sufficient.

Galvanic current, which can be read as a small ohmic drop across a little resistor inserted in the external cable, is expected to increase from I_{g0} to I_{gb} during biofilm formation and then to decrease if an effective antifouling procedure is applied

Information on the development of the biofilm are obtained from the trend of I_g .

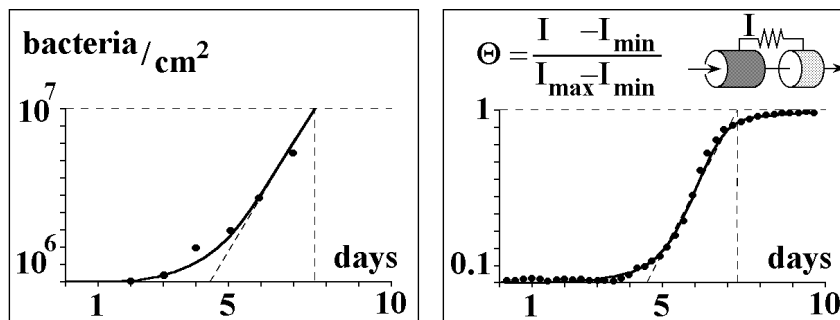
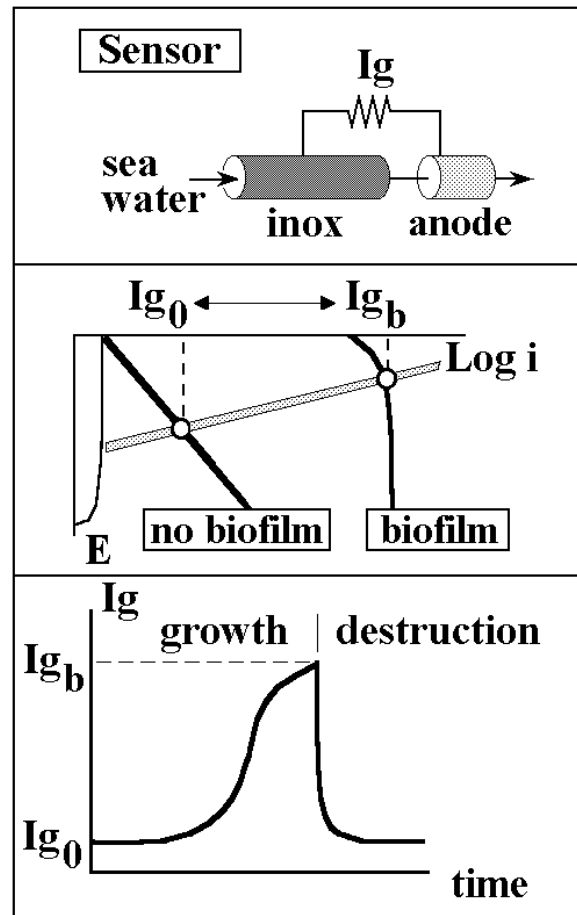


Fig 4 - Although very simple, the electrochemical device shown in figure 3 is extremely sensitive to the biofilm growth.

Figure 4 shows, on the left side, the evolution of the bacteria mean population density on SS surfaces obtained from SEM count of settled bacteria on SS samples exposed in a loop in which natural seawater flowed.

On the right side of the figure the trend of the current generated by the sensor put in series in the same loop is plotted.

By comparison of the two graphs it follows :

- the electrochemical sensor provide correct information on the incubation time and on the growing rate of the biofilm
- the electrochemical sensor signalizes a biofilm amount in the order of 10^6 bacteria/cm² (surface coverage in the order of a few percent),
- the signal of the electrochemical sensor is saturated when biofilm reaches a bacterial population in the order of 10^7 bacteria/cm² (coverage still far to be complete).

Fig 5

Qualitative comparison between the sensitivity of the electrochemical sensor and that of “classical” biofilm sensors based on friction factor or heat exchange (known to be insensitive to biofilm amount less than about 30-40 μm).

It suggests that only electrochemical sensors provide good information on the first, crucial, phase of the biofilm growth and that, as a consequence, these sensors can be applied to optimize the application of antifouling procedure.

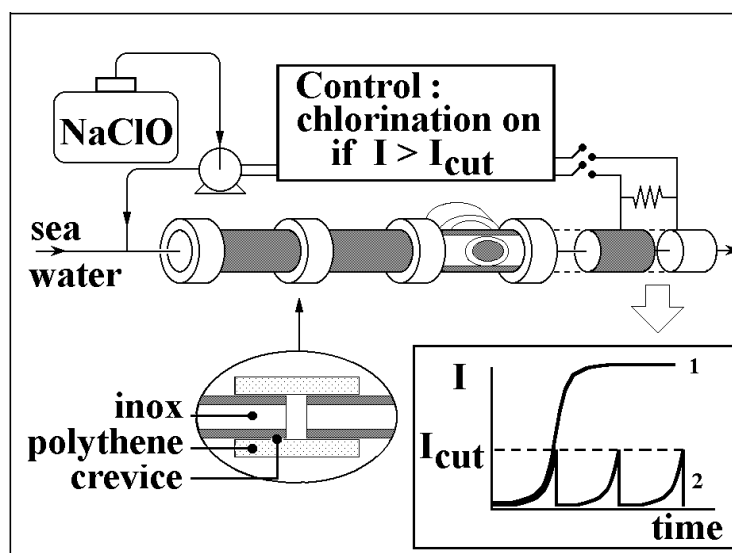
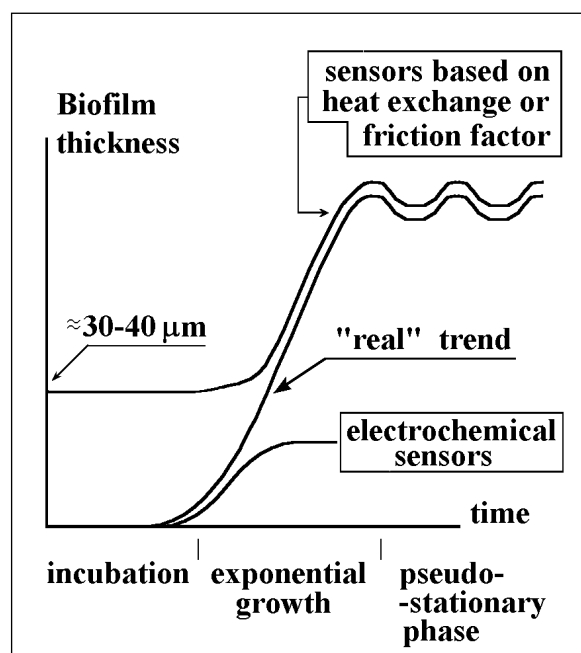


Fig. 6 Figure shows the scheme of two loops utilized for the tests whose results are shown in the figures 7, 8 and 9.

In both the loops several AISI 316 SS pipes, on which crevices were intentionally created at both the extremities, were put in series with an electrochemical biofilm sensor.

In the first loop natural untreated seawater flowed inside the pipes.

In the second loop the sensor was utilized to automatically guide the application of a standard chlorination (0.5 ppm for 0.5 hours) : chlorination is applied when the signal provided by the sensor overcomes a prefixed limiting value I_{cut} .

Aim of the tests was to see if the sensor, without maintenance, is able to automatically apply antifouling procedures in such a way that, concurrently :

- the biocide addition is minimized (fig. 7),
- the SS surfaces are maintained clean (fig.8),
- MIC is minimized (fig.9).

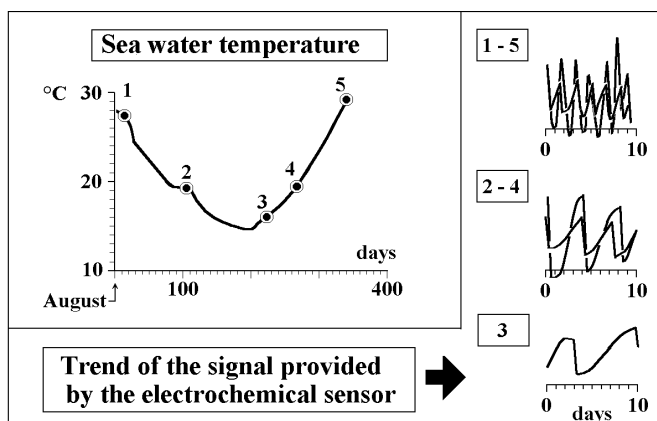


Fig.7 - During a test lasted one year, in which seawater temperature ranged from 28 to 14 °C, the sensor “decided” to change in time the chlorination frequency of the applied antifouling procedure, automatically following the change of the biological activity induced by the temperature variations. As an example, only one chlorination every about 6 days was judged sufficient during the winter.

Fig. 8

Figure shows that, after three months of exposure, the internal walls of the pipes exposed to automatically treated seawater are totally clean (right side). On the contrary, a thick biofilm layer is present on walls of SS pipes exposed to untreated seawater (left side).

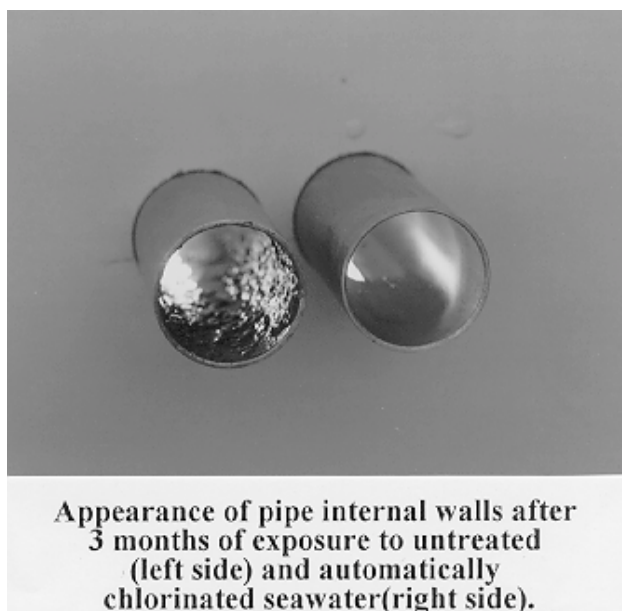
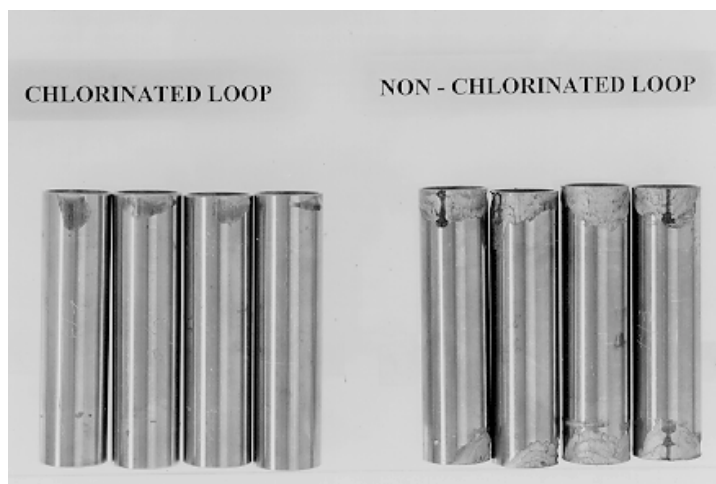


Fig. 9

Figure shows that only a superficial attach was observed on one side of the pipes after 3 month of exposure in automatically chlorinated seawater (left side). On the contrary heavy attaches, till perforation of a pipe wall 1.2 mm thick, are observed on both the extremities of the pipes exposed to untreated seawater (right side).



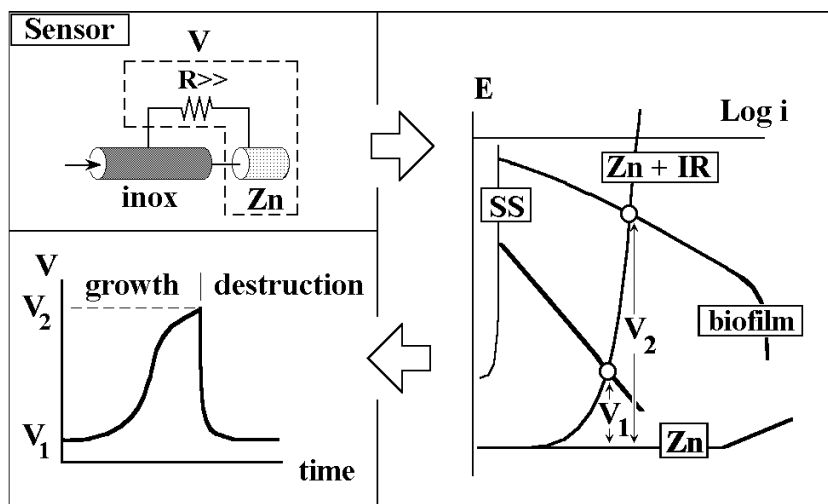


Fig. 10 - A new version, now patented by ENEL, of the electrochemical sensor shown in figure 3.

In comparison to the sensor shown in figure 3 the anode is, now, substitute with zinc and the resistor on the external circuit is high in so far that the sensor causes a quasi-intentiostatic cathodic polarization of the SS surface. The biofilm growth is indicated by the increase of the ohmic drop across the resistor.

This new version of electrochemical sensor can be applied not only in seawater but in fresh waters, too.

Conclusions

The electrochemical sensors of biofilm based on the effect of “cathodic depolarization” offer the following advantages :

- extremely simple configuration ;
- low cost ;
- no maintenance (specially in the final version) ;
- they provide information in real time and in continuous without electrical power supply ;
- specific for the biofilm fraction of a fouling ;
- extremely high sensitivity in the first phase of the biofilm growth (or in the final phase of the biofilm destruction) ;
- they signalize, concurrently, the risk of MIC :
- the meaning of the provided signal can easily be understood also by not specialized people ;
- the provided signal can be used to rationalize the application of antifouling procedures in plants saving efficiency, decreasing corrosion and concurrently minimizing biocide additions in water ;
- in the new version, sensors can be applied, with the same configuration, not only in seawater but also in fresh waters ;
- in the new version, sensors can be arranged in order to concurrently signalize both biofilm growth on the sensor surface and the residual chlorine in water at concentration between 0.2 and 1 ppm.

In- field experience

On-line monitoring of chlorination treatments by BIOX system in power plants

Pierangela Cristiani, CESI, Italy.

The BIOX^P on-line biofilm monitoring system has been operating at the Vado Ligure power station experimentally for two years, in order to control and improve, the chlorination treatments of seawater-cooled steam condensers.

After the introduction of BIOX monitoring, the intermittent chlorination treatment adopted at Vado Ligure power plant was generally effective to keep condenser tubes clean from biofouling.

Following the positive experience at the Vado Ligure power plant, the use of industrial BIOX system is extending to the others ENEL power plants for the optimization of the chlorination treatments.

All the plants adopting BIOX monitoring system got technical and economic benefit from the optimisation of chlorination treatments.

REFERENCES

- 1) Cristiani, G. Bianchi, “Microbial Corrosion Prevention in ENEL Power Plants”, Microbial induced Corrosion, n. 22, European Federation of Corrosion Publications, The Institute of Materials ISSN 1354-5116, London, 1997.
- 2) Cristiani, A. Mollica, G. Ventura, “On-line monitoring of biofilm and T.R.O. by a new ENEL system, “Understanding Heat Exchanger Fouling and Its Mitigation” conference proceedings, 11-16 maggio, Lucca, 1997.
- 3) Cristiani, F. Agostini, “On-line monitoring of chlorination treatments at Vado Ligure power plant by BIOX system: two year of experience”, “Mitigation of heat Exchanger Fouling and its Economic and Environmental Impact”, July 11-16, Banff, Alberta, Canada, 1999.

BIOFOULING IS A SEVERE PROBLEM IN POWER PLANTS

ENEL spends millions dollars per year for:

- the reduction of condenser performances caused by fouling
- the prevention of biofouling and microbial corrosion.



Roughly 50% of the damages on condenser tubes might be prevented improving the cleaning during the plant operation.



CLORINATION TREATMENTS CONTROL

The Italian law allows **0.2 mg/l** as maximum value of chlorine concentration admitted at the discharge.

THE TRADITIONAL APPROACH

(skilled personnel necessary)

- Periodical biological examination
- Periodical chemical analysis
(chlorine concentration and water chlorine demand as Total Residual Oxidant)

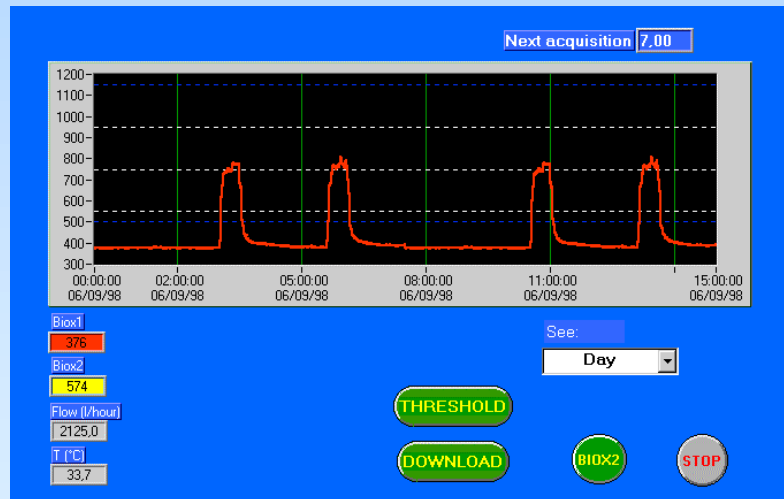
THE NEW APPROACH

- **BIOX Electrochemical on-line monitoring**

BIOX system

New approach in chlorination treatment control

BIOX system employs a new simplified version of electrochemical biofilm sensor. Its response is correlated to the changes of electrochemical kinetic processes on metal surfaces induced by bacteria settlement or by oxidant agents.

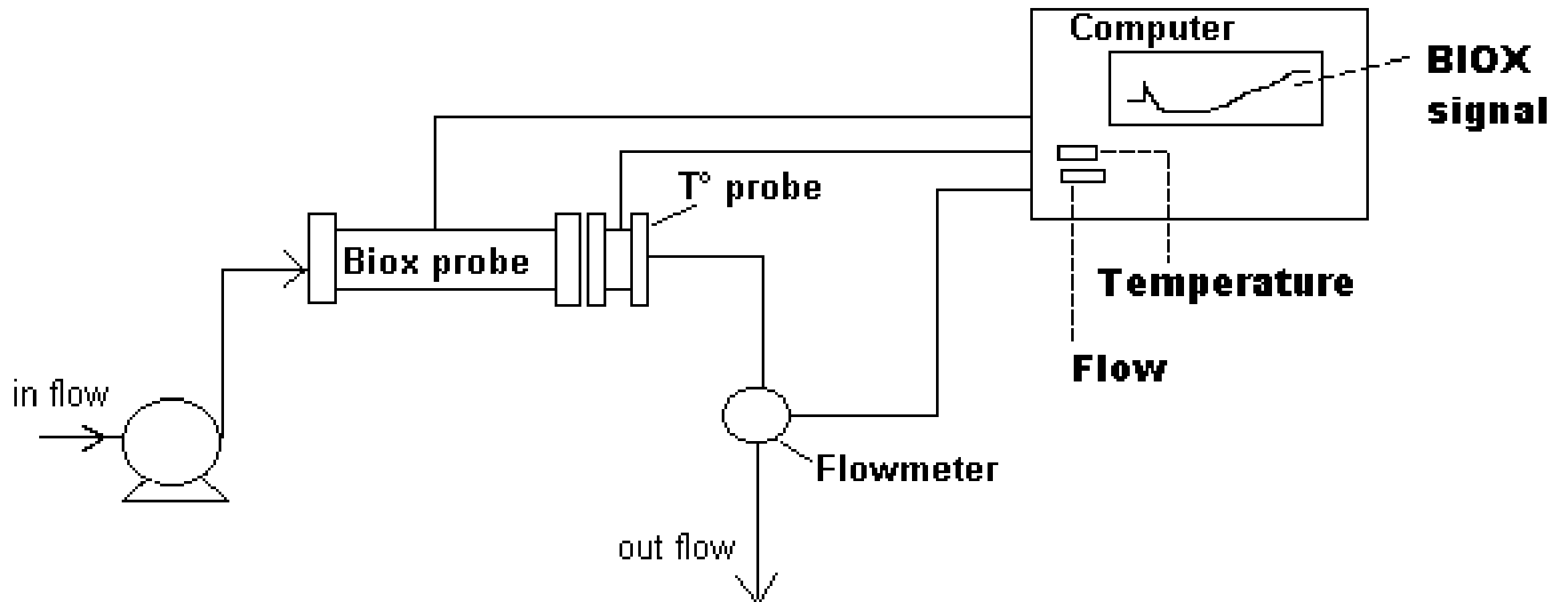


The probe sensitivity is close to

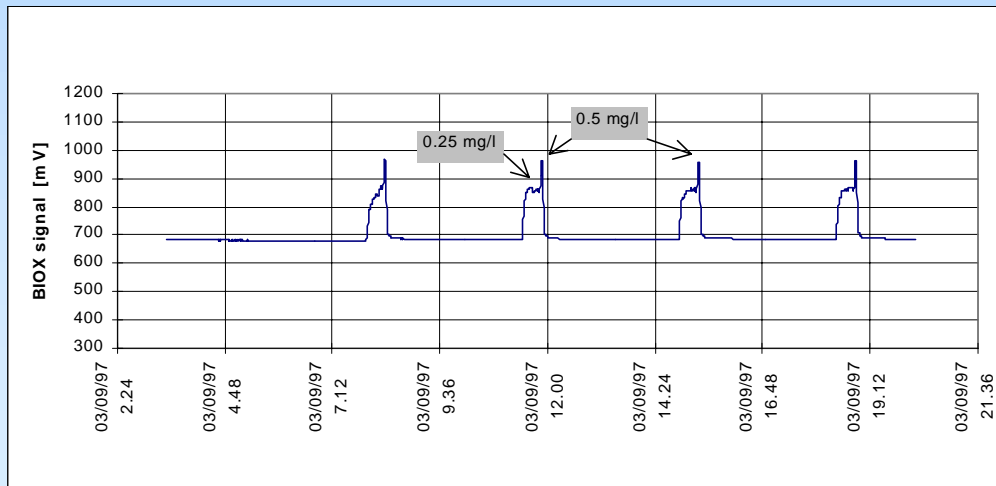
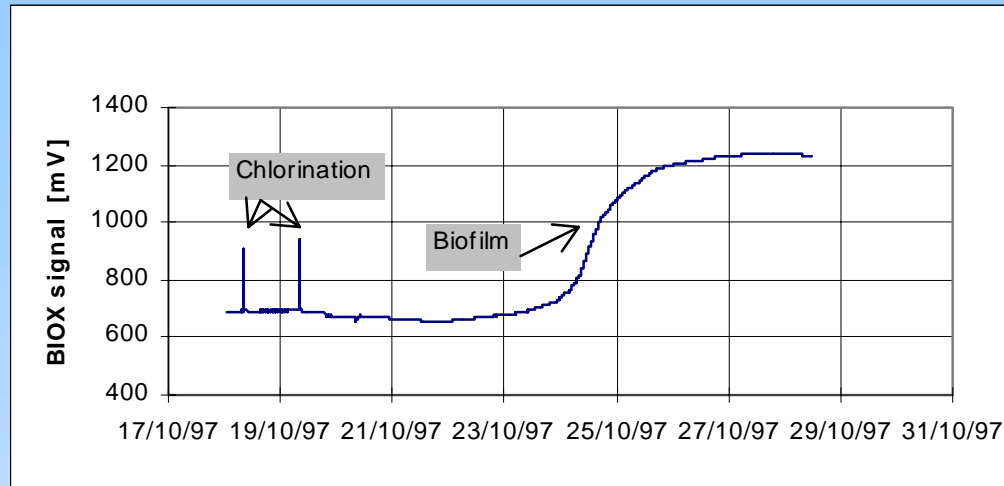
- *10^6 bacteria/cm²*
- *0.1 - 1 mg/l as T.R.O.*

The response of sensor permits to have, a direct index of biofilm growth and the effective oxidants concentration on the sensor surface.

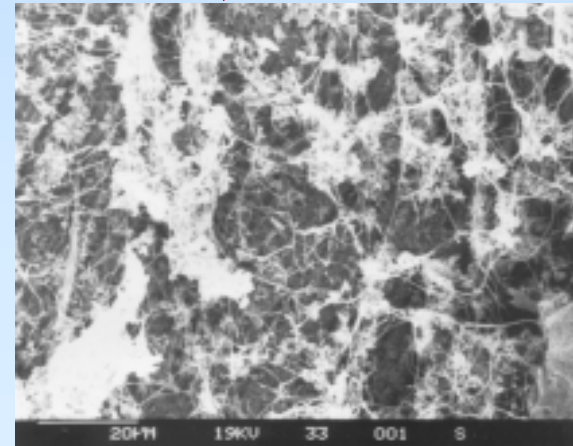
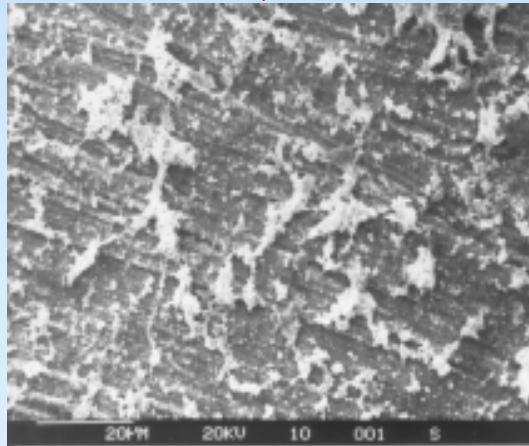
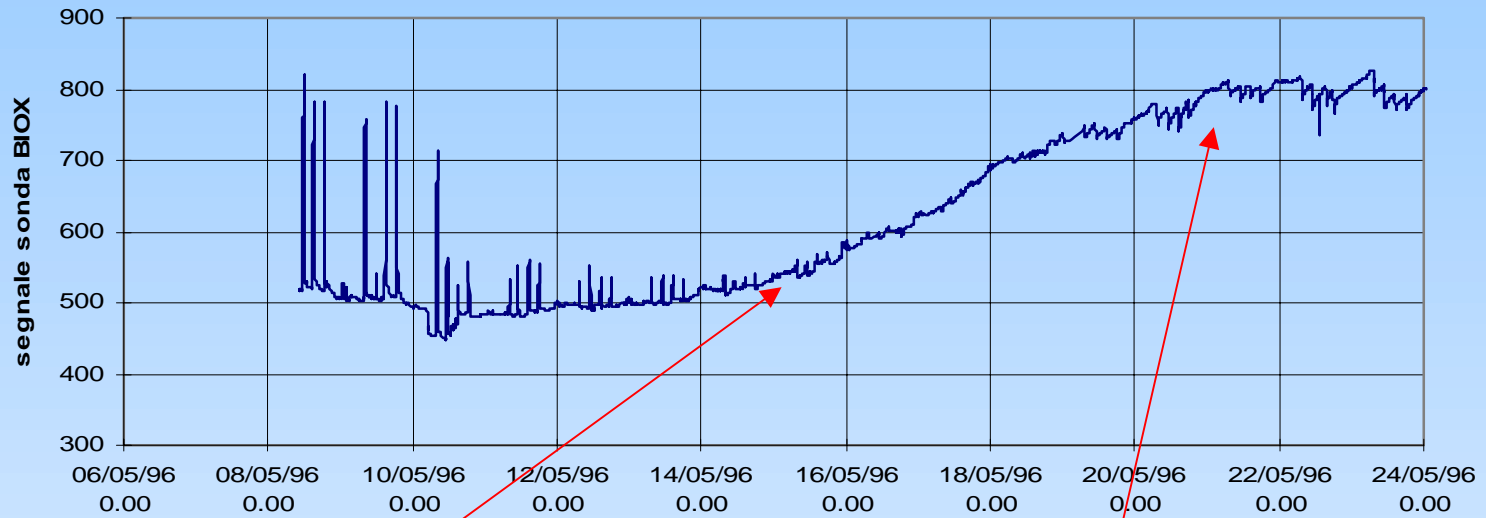
BIOX system

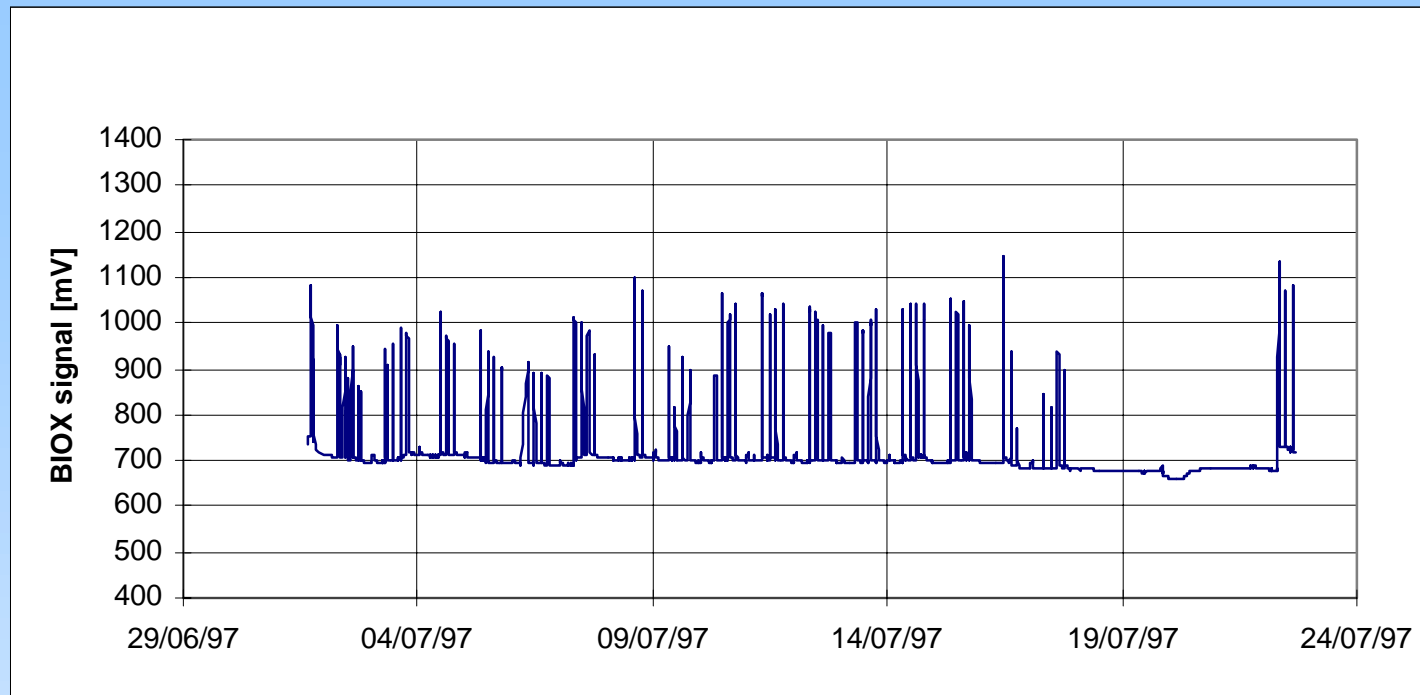


BIOX signal explanation

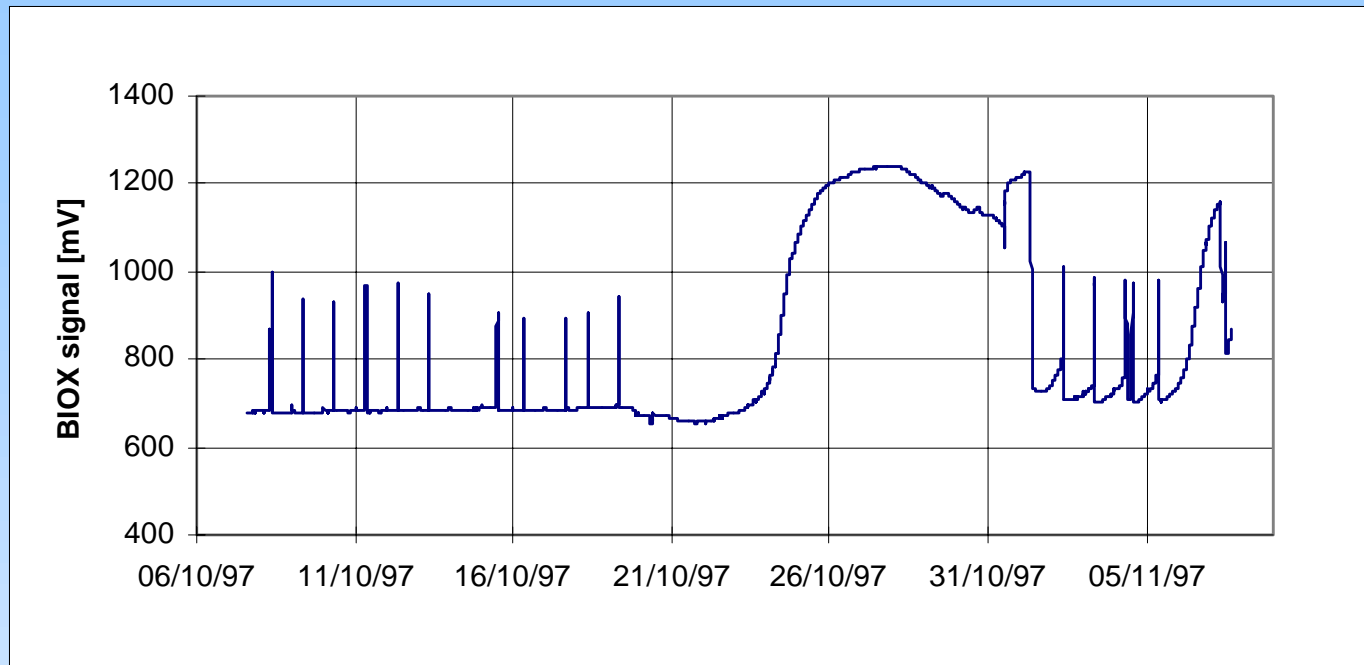


Biofilm growth on BIOX sensor at different signal level





In-field experimental data from Vado Ligure power plant: BIOX output shows the effectiveness of the intermittent chlorination treatment adopted to prevent the biofilm growth in July 1997.



BIOX output on 20 October: a decrease of the flux in the cooling loop caused the biofilm growth and the previous treatment were not strong enough to control the growth.

CONCLUDING REMARKS

- The BIOX system showed a very good performance to monitor biofilm growth and chlorination treatments and can be employed to minimize the biocide quantity, reducing the treatment as duration and concentration which are strictly necessary to inhibit the biofilm growth.
- In the first monitoring experience by BIOX system at Vado Ligure power plant, an intermittent chlorination treatment has been optimized and resulted generally cheap and effective to keep condenser tubes clean from biofouling.

MICROBIOLOGICALLY INFLUENCED CORROSION MONITORING:

CEA PRACTICE

D. Féron & M. Roy
CEA - Laboratoire d'Etude de la Corrosion Aqueuse

BRITE EURAM thematic network workshop
“biofilm and MIC monitoring: state-of-the-art”

Venetia (Italy), 13th April 2000



Laboratoire d'Etude de la Corrosion Aqueuse

LECA/16751/00-DF

CEREM

Background of MIC monitoring in CEA laboratories or facilities

- Objectives:
 - R&D investigations
 - Early detection of corrosion failures
 - Efficiency of countermeasures

- Specific conditions:
 - Monitoring system has to be “safe” (no introduction of pollutants, long term operation, ...)
 - Passive materials (stainless steels)
 - “Nuclear environment”

- Monitoring devices
 - developed for pipe systems in the middle of the 80^{ies}
 - in batch systems, operating since mid-1995

Background of MIC monitoring in CEA laboratories or facilities (cont'n)

➤ Monitoring includes

- ❖ Water chemical and physical measurements such as:
 - Temperature,
 - pH, Ct, oxygen concentration,
 - Main anions and cations, organic matters,

- ❖ Corrosion measurements such as:
 - Free corrosion potentials,
 - Polarisation resistance, impedance measurements,

- ❖ Microbial measurements such as:
 - Planktonic and sessile bacteria
 - Bacteria identification

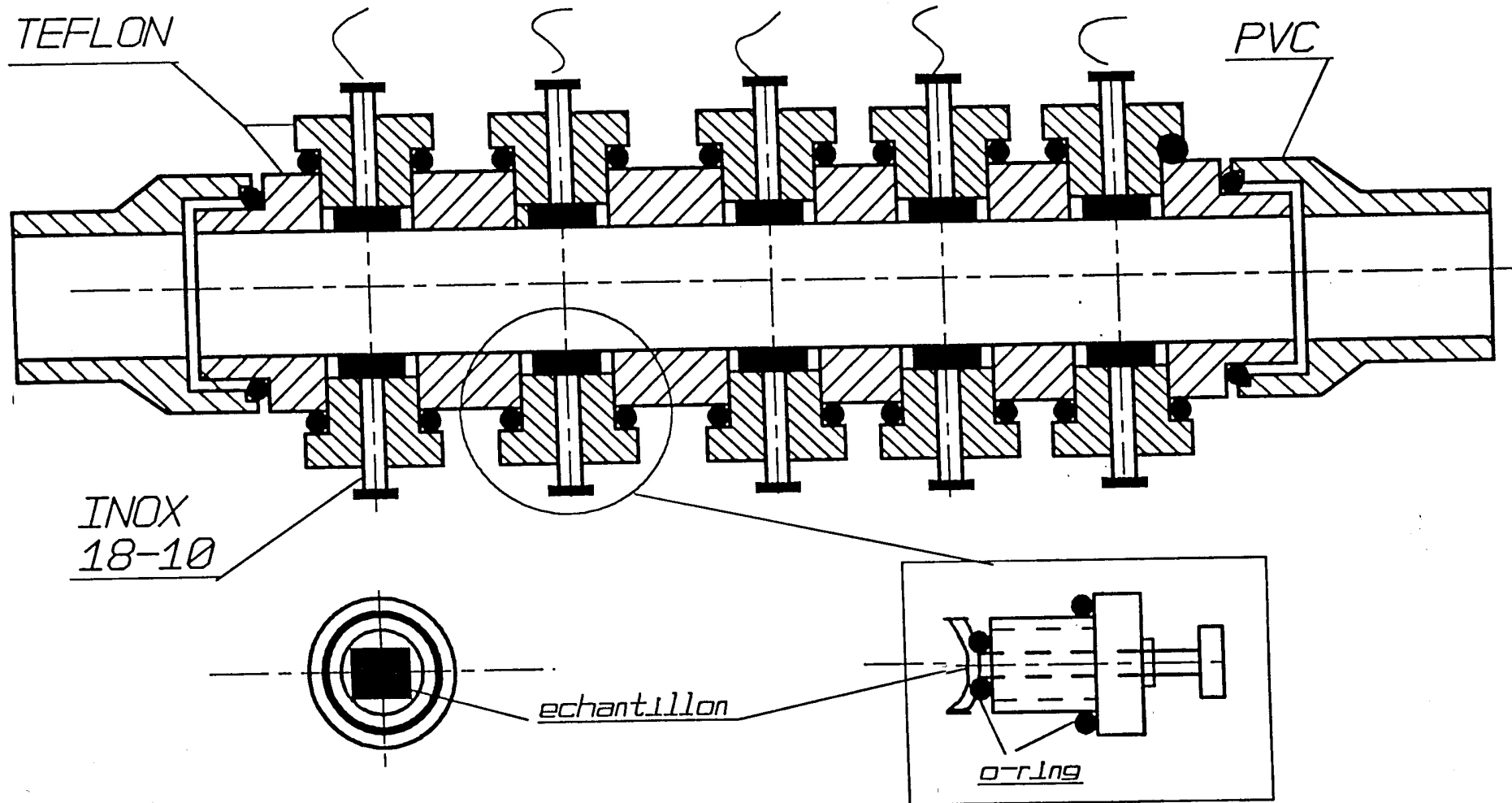
MIC specific monitoring devices at CEA

- Monitoring devices includes
 - Classical “laboratory” electrochemical equipment (from millivolmeters to impedance equipment when needed)
 - Material specimens (stainless steels) which are used as electrodes and corrosion coupons
 - Reference electrodes or pseudo reference electrode

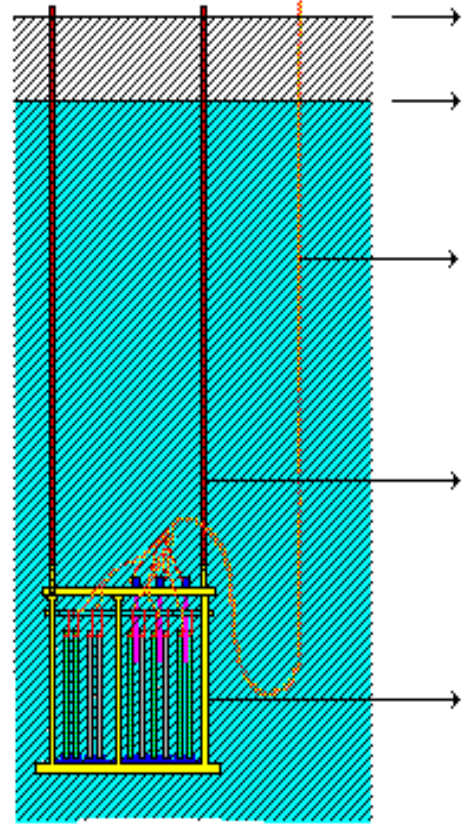
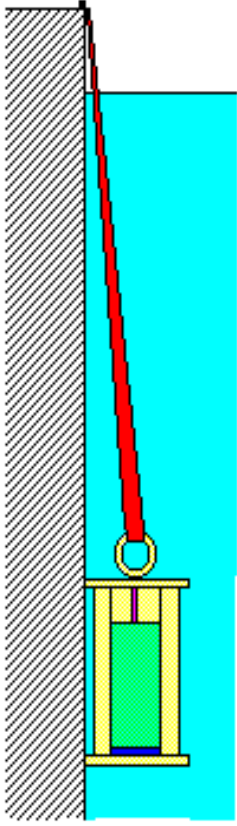
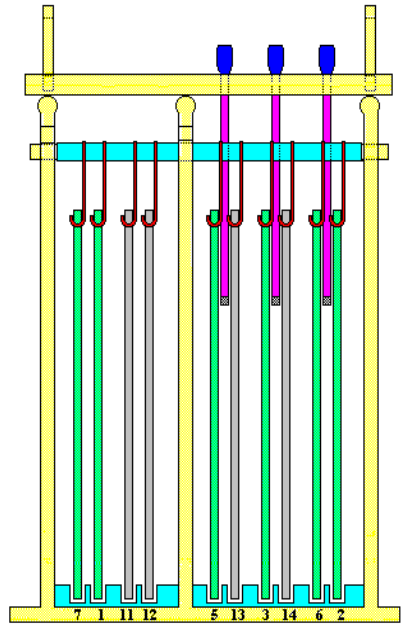
- Two monitoring devices are in use:
 - “Clarinet” in tubing systems,
 - “Rack plate device” in batch systems

- Monitoring includes
 - to follow water parameters
 - to collect data with the monitoring device
 - to remove coupons for biofilm analyses and coupon observations

CLARINETTE device



RACK plate device



Niveau de l'eau

Câble de liaison

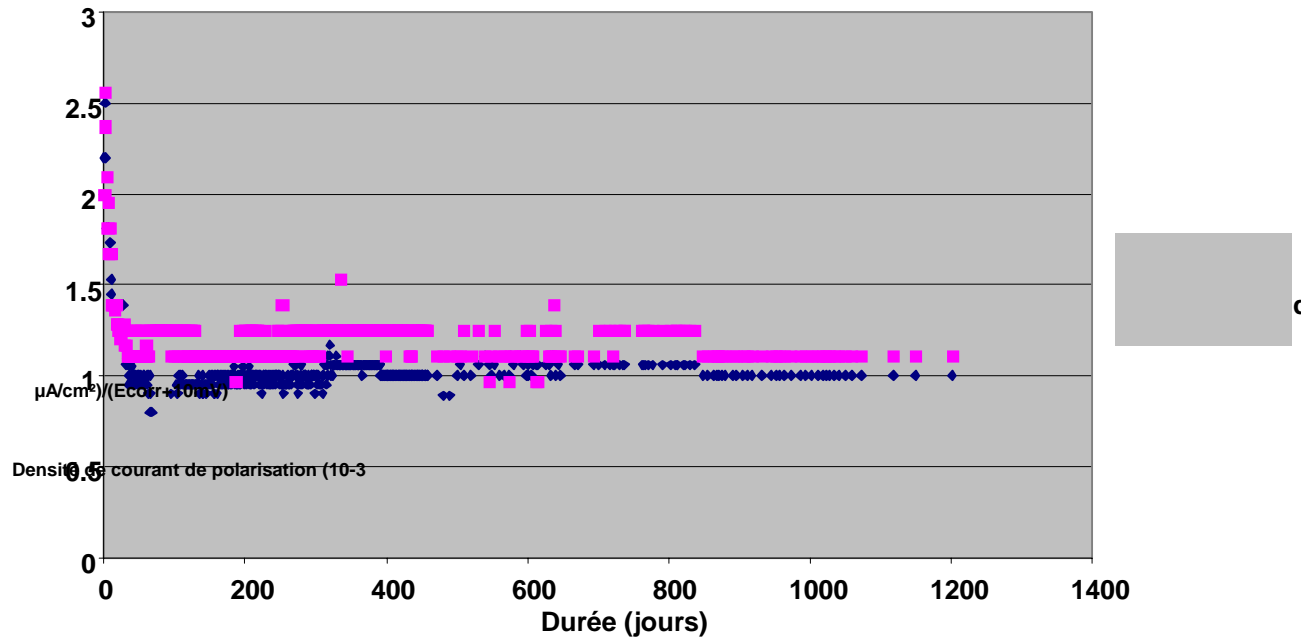
Sangle

Dispositif

- Acier 304L
- TEFLON
- Electrodes 304L
- Electrodes 304L + cordons de soudures
- Crochets titane
- Electrodes de références

Long-term evolution:

Polarisation current (+10 mV/ E_{cor}) of stainless steel specimens in “fresh” water over more than 3 years



MIC specific monitoring comments

➤ Microbial monitoring

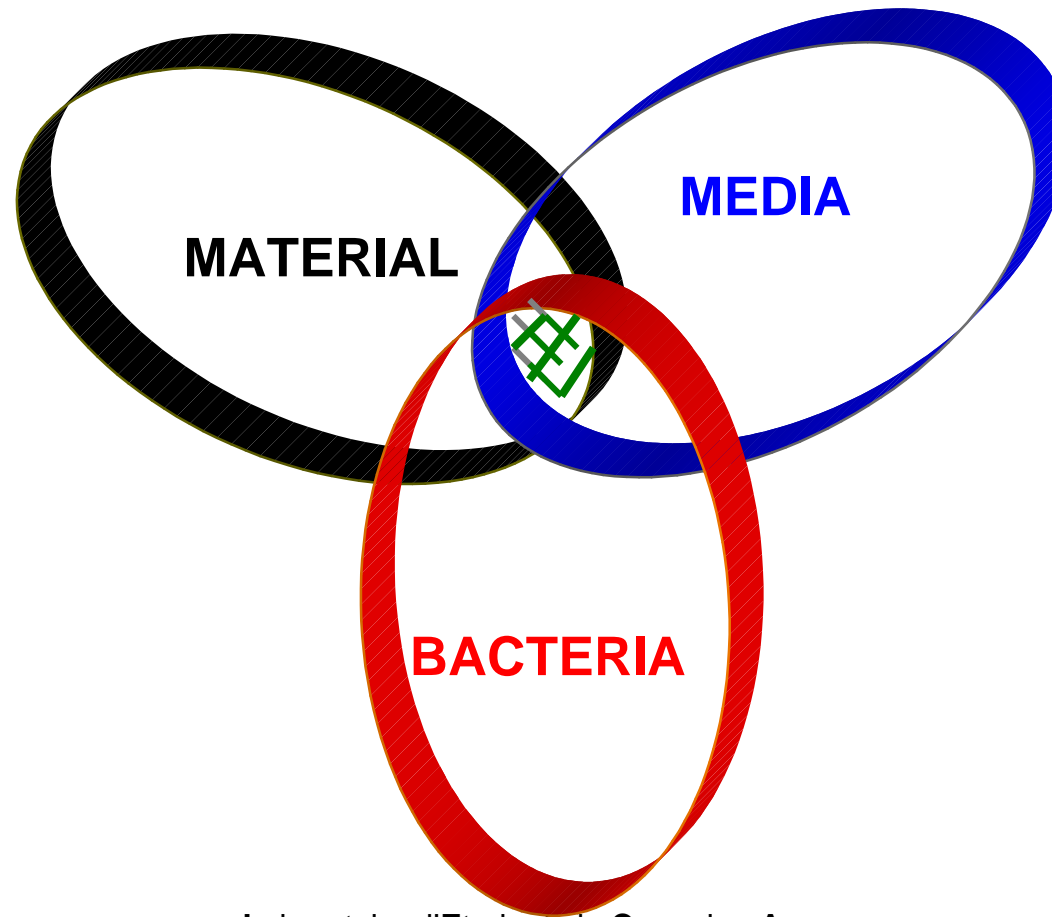
- Samplings need to be performed by a microbiologist
- Numbers and species of planktonic bacteria are highly “fluctuating”
- No “absolute” values (only orders of magnitude)
- Sessile bacteria sampling have to be “representative”
- There are no “corrosive” bacteria and “non corrosive” bacteria

➤ Data collection

- All data may be important for corrosion behaviour (temperature, ratio $\text{Cl}^-/\text{NO}_3^-$,)
- Biocide analyses (Chlorine, O_3) need to be performed very rapidly after the sampling
- Evolution of parameters is more important than the instantaneous values

Conclusive comment

Microbiological Influenced corrosion monitoring is a “classical” corrosion monitoring with one more “actor”: bacteria



Corrosion monitoring

Purpose:

Corrosion control

Assessing the condition of the facility

Avoiding break downs and unplanned repair and service stops



Corrosion rate

Reliable measurements

On-line

Real time

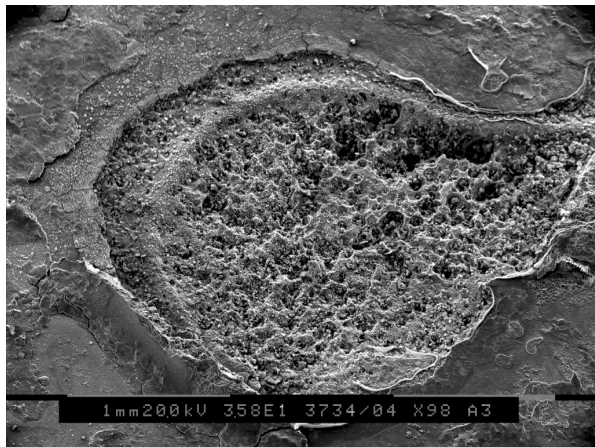
Qualitatively registering changes

Detection of biofilm and deposits

Non-destructive

Simple analysis

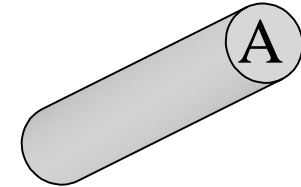
Economically feasible



Weight loss (coupons) and electrical resistance ER - direct measure of the physical metal loss

$$V_{\text{corr}} = \frac{m_{\text{initial}} - m_{\text{after}}}{A \cdot \Delta t}$$

$$R = \frac{\rho \cdot L}{A}$$



↑ simple
widely used techniques
standardised
applicable in all media
visual examination of coupons

↓ sensitivity normally low
historical data
sudden changes cannot be detected
weight loss is destructive technique

sensitivity of ER can be improved by design and better instrumentation

Linear polarisation resistance technique LPR

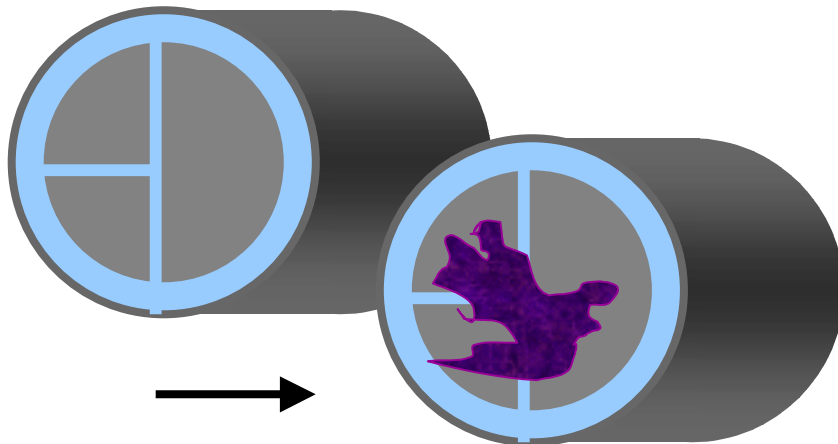
Assumptions:

linearity at the corrosion potential $R_p = B/i_{\text{corr}}$

high conductivity

÷ other electrochemical reactions

low capacitive current: $i = i_F + i_c = i_F + C^*dE/dt$

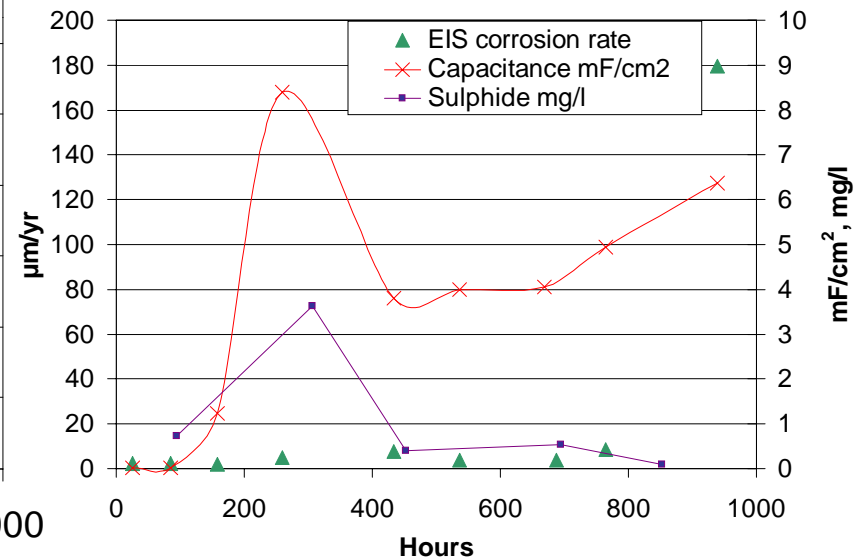
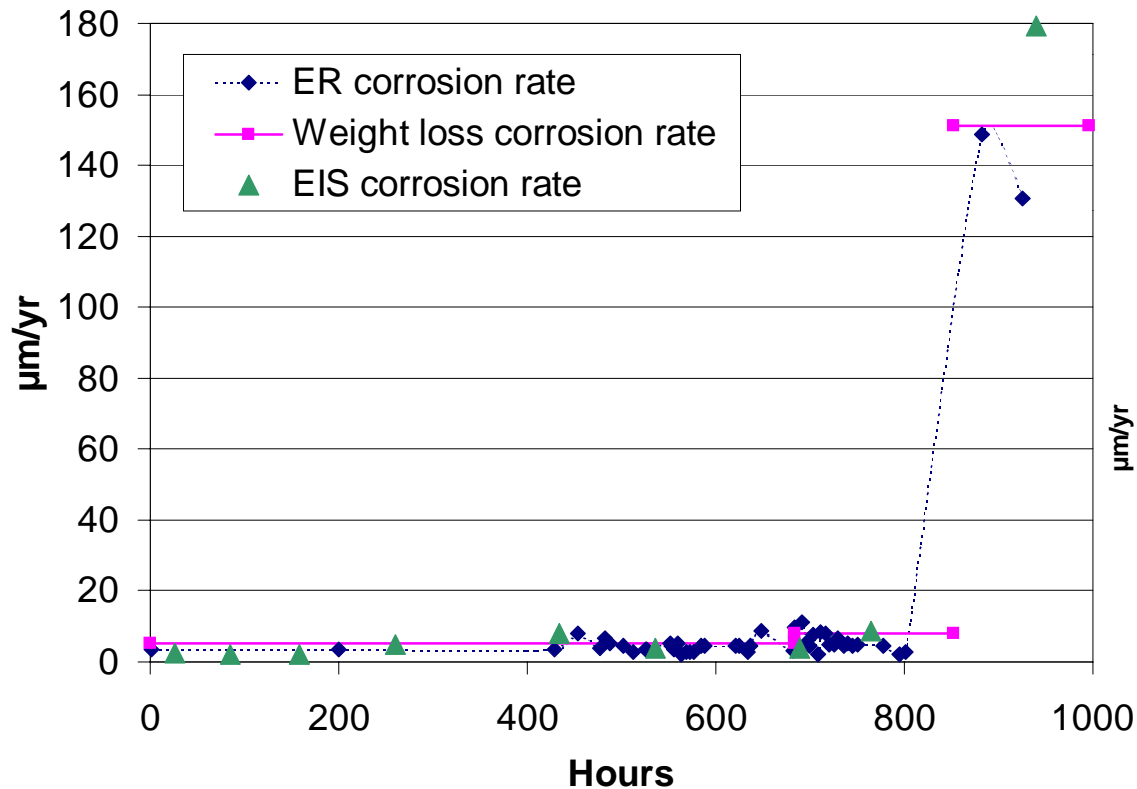


Short circuiting by deposits

LPR is not recommendable for MIC:

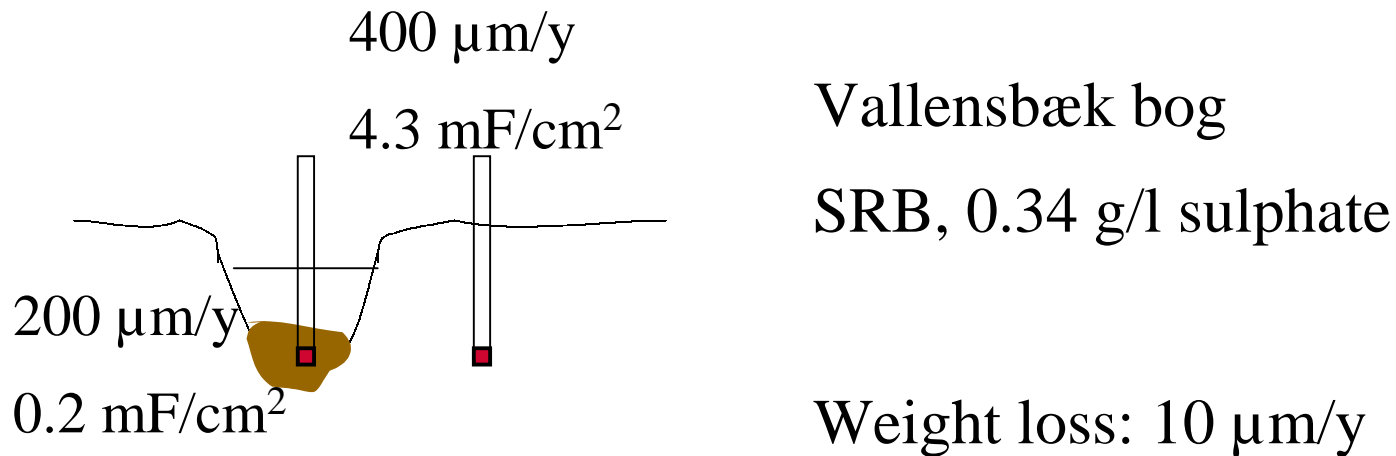
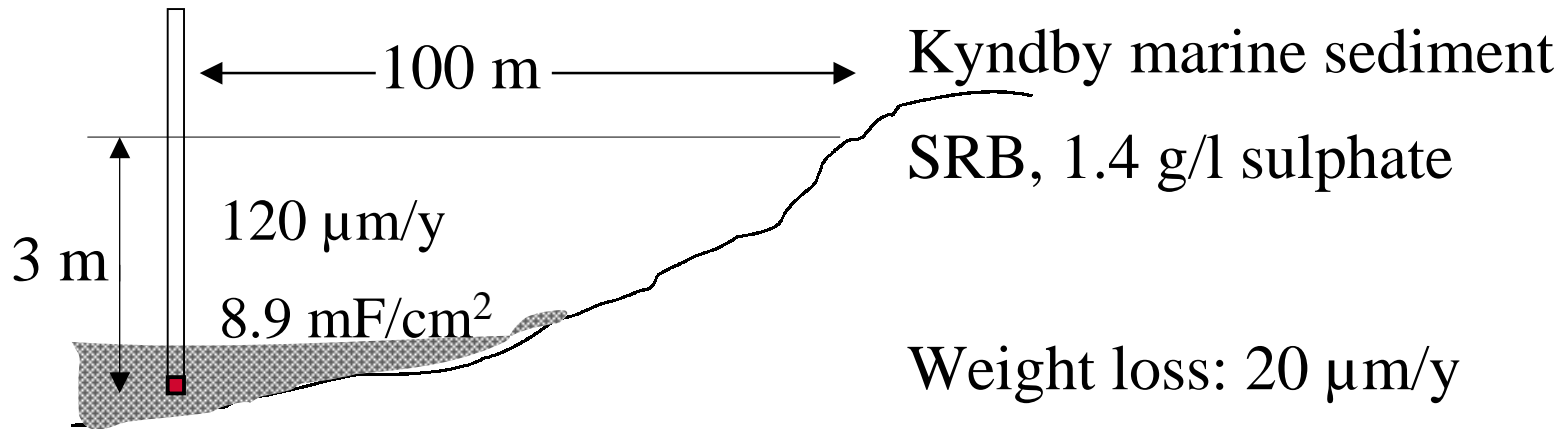
- Electrochemical reactions (ferrous sulphide)
- Deposit formation
- High capacitive current contributions

ER, EIS and weight loss correlate for protective sulphide films



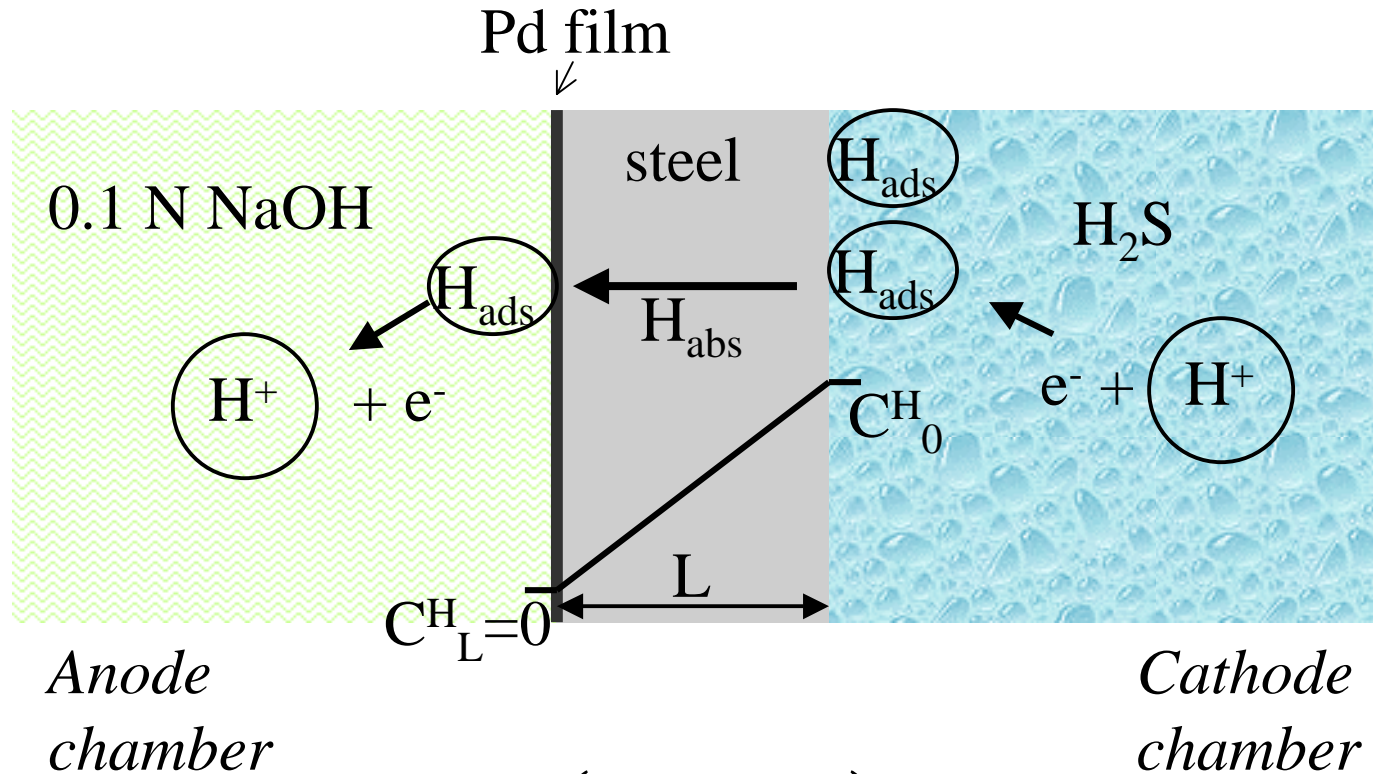
Corrosion rate without stirring (0-700 timer), slow stirring (700-850 hr) and during passive aeration (850-1000 hr) in SRB active media.

Corrosion rate is overestimated by EIS under high SRB activity



L.V. Nielsen, 1998

Hydrogen permeation can be measured electrochemically

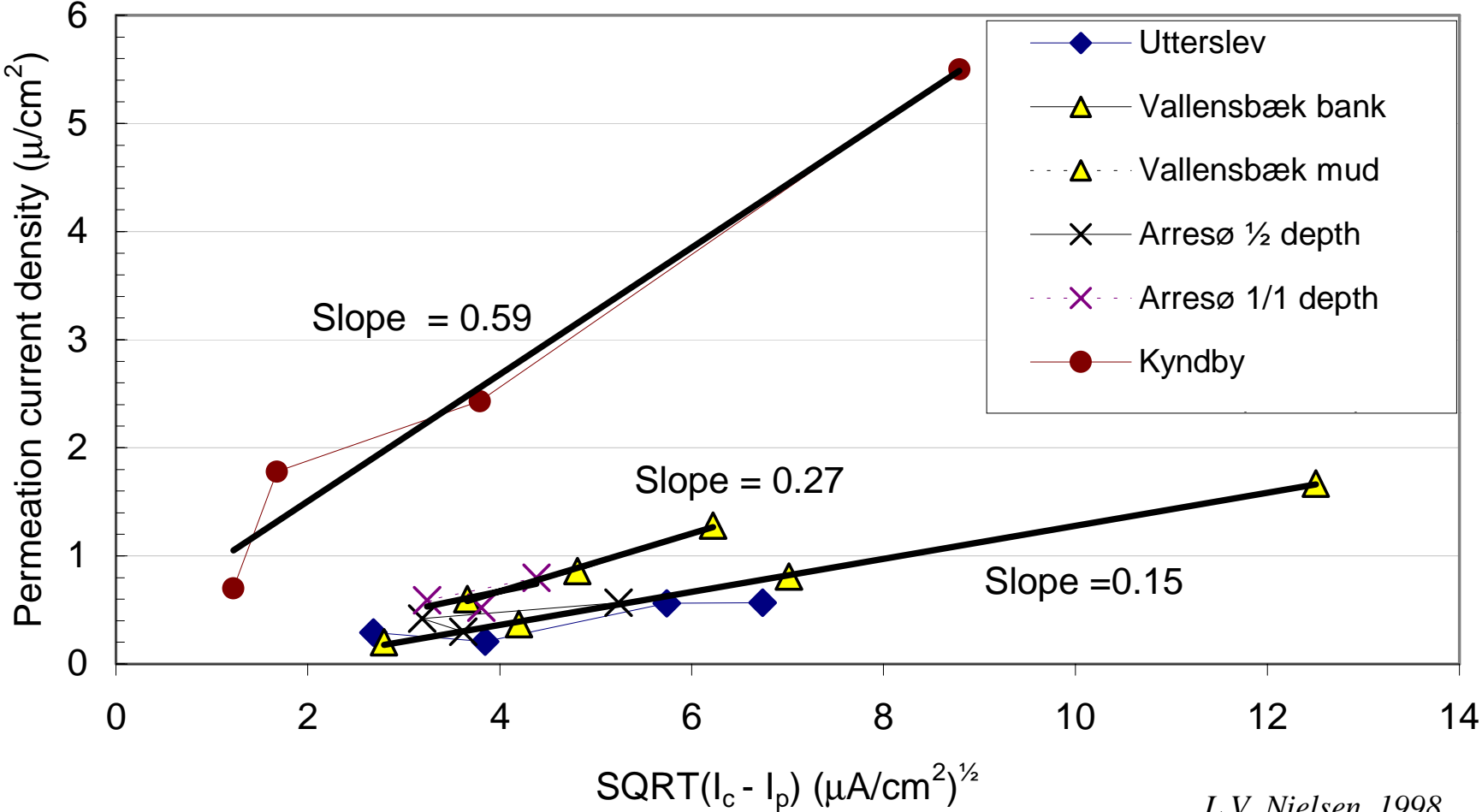


$$I_{perm\infty} = \frac{(C_L^H - C_0^H) D_{eff} F}{L}$$

Biofilm and H_2S can increase hydrogen permeation

Degree of hydrogen permeation increases with increasing SRB activity

Hydrogen permeation - IPZ model.



L.V. Nielsen, 1998

Monitoring MIC of carbon steel in H₂S or SRB media

Corrosion rate cannot be measured reliably by electrochemical techniques - LPR and EIS

Reliable corrosion rates are measured by weight loss or ER
The ER technique can be refined

EIS and ENM can be applied for monitoring mechanisms and localisation

Optical Fouling Monitors

Dr RL Wetegrove, Dr RH Banks

III General Meeting - Biocorrosion Network

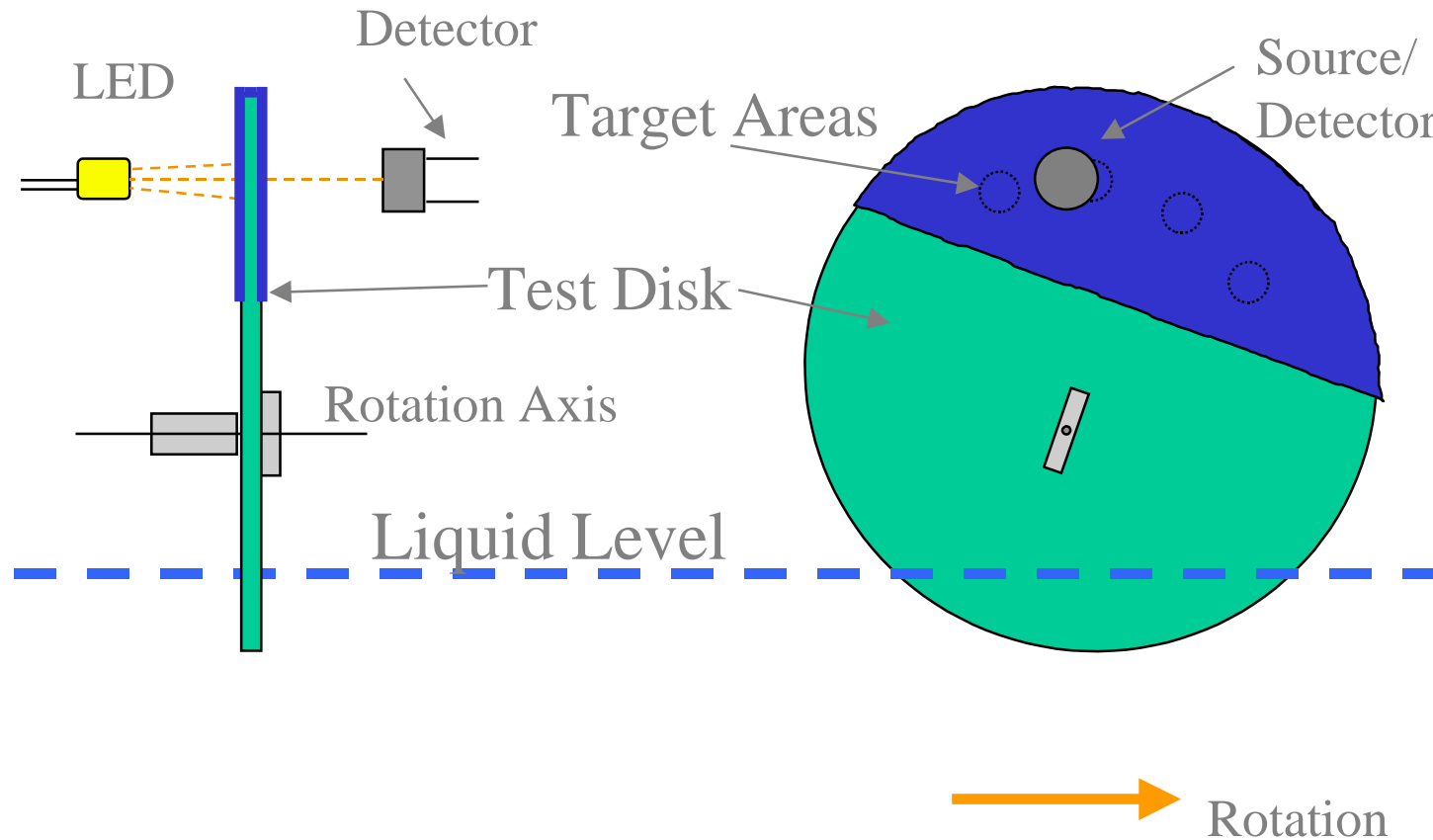
Workshop on Monitoring Systems

Venezia 12-14 April 2000

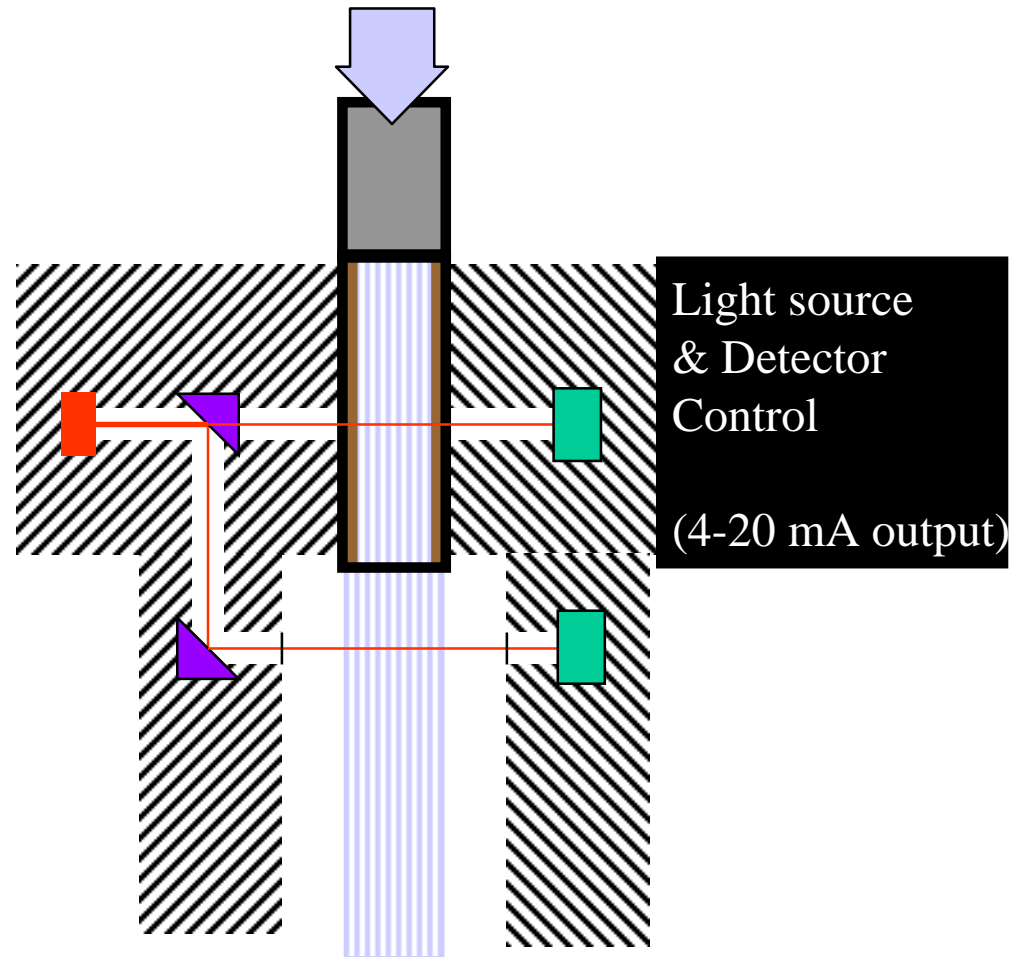
Nalco Optical Monitors

- Five Patents:
 - Disk Monitors
 - Reflectance (US 5,264,917)
 - Transmittance (US 5,155,555) Paper
 - Wiper Monitor (US 5,185,533) Cooling Water
 - Falling Stream (US 6,023,070)
 - Living Deposits Detection (US 5,796,478)
- One Standardized, One in Development

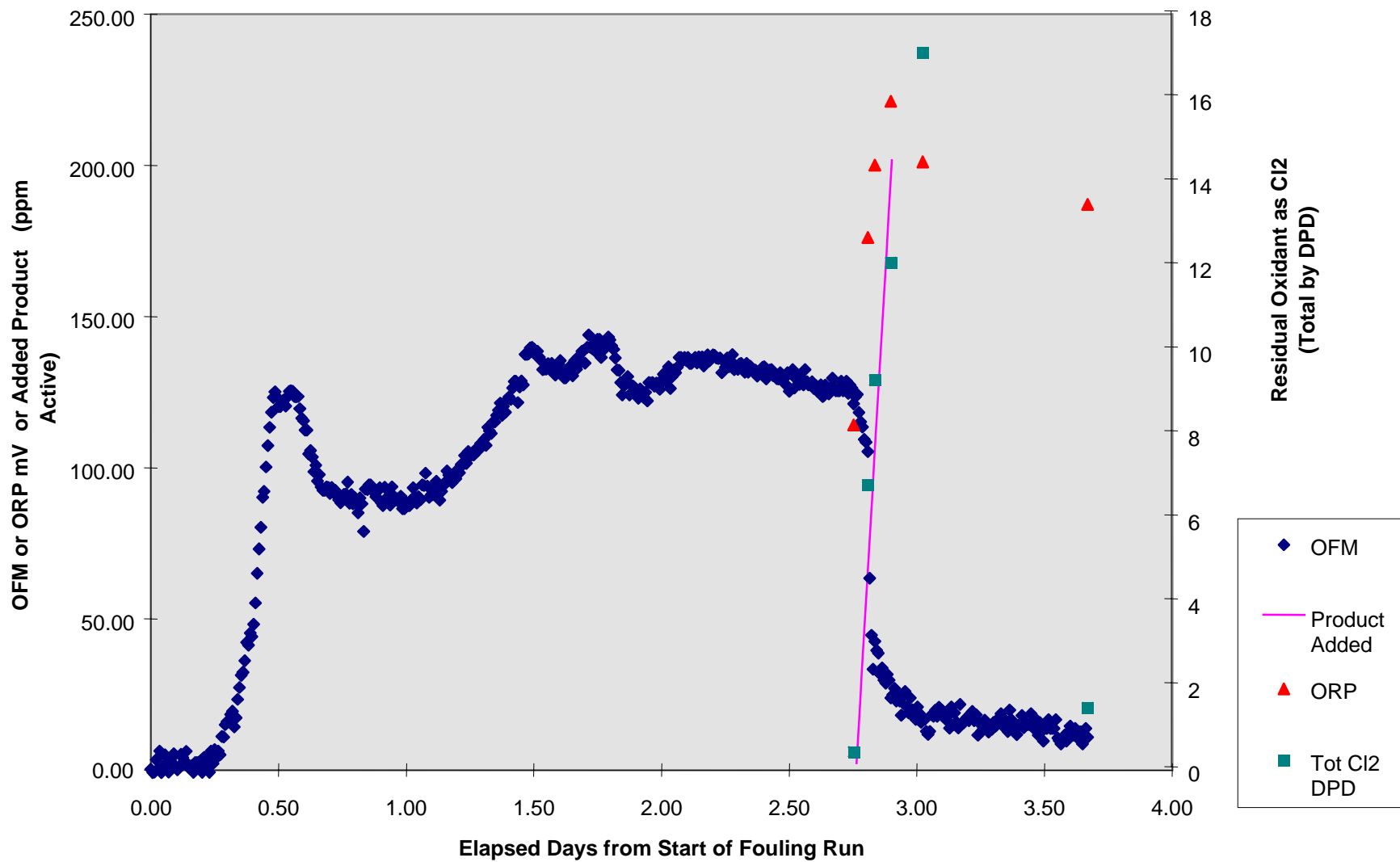
Disk OFM in Read Position



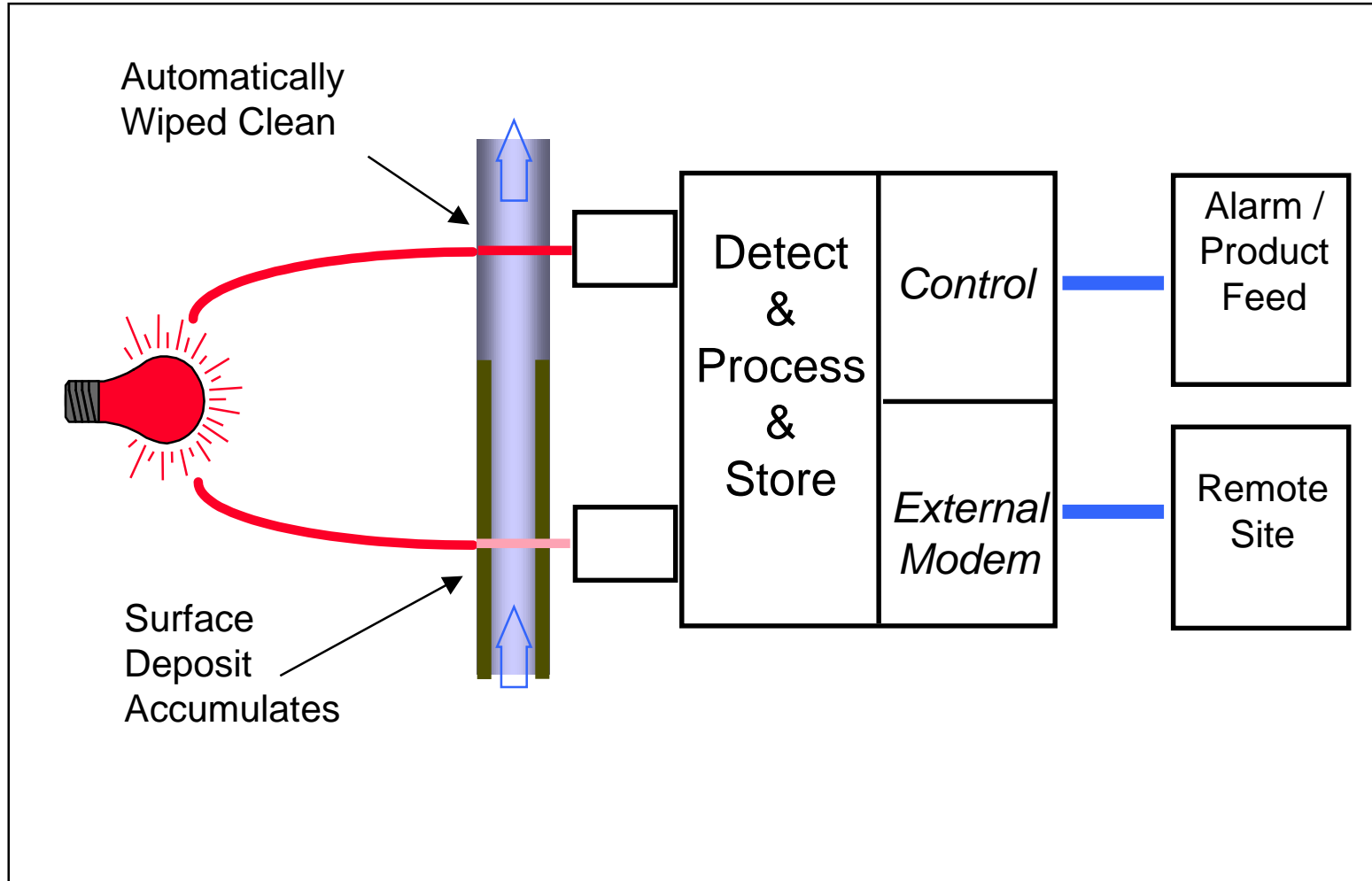
Falling Stream OFM



Nalco Falling Stream Monitor Results



Wiper OFM



ORP & Fouling Monitors -- March to June

