018207
CORRLOG
Automated corrosion sensors as on-line real time process control tools

SIXTH FRAMEWORK PROGRAMME
HORIZONTAL RESEARCH ACTIVITIES INVOLVING SMES
CO-OPERATIVE RESEARCH

Publishable final activity report

Period covered: from **01/09/2005** to **29/02/2008**
Date of preparation: **07/04/2008**
Revision: **1**

Start date of project: **01/09/2005** Duration: **30 months**

Project coordinator name:
Dominique Thierry

Project coordinator organization name:
Institut de la Corrosion (ICO)

Automated corrosion sensors as on-line real time process control tools
CORRLOG

A research project supported by the European Commission under the Sixth Framework Programme Horizontal Research Activities involving Small and Medium Enterprises – Co-operative Research (CRAFT)

Duration: 09/2005–02/2008 Contract number: 018207

www.corrlog.com

BACKGROUND

In developed countries, direct corrosion losses reach approximately 3–5 % of the gross national product. This immense number represents the loss by 50 times higher than direct annual losses caused by fires. Corrosion expenditures could be radically reduced if monitoring of corrosion became a natural part of the decision making processes. However, for the time being, corrosion measurements in process plants, soils, or atmospheric conditions are usually a part of expert-conducted surveys, the results of which are presented to end-users in written reports. This project is based on the **need for implementing corrosion sensors as process control tools**, because the information on actual corrosivity of the environment is crucial for effective corrosion protection. Implementation of on-line and real time monitoring enables operators to take immediate counter measures if corrosion is accelerating, and thus decrease the corrosion costs. Properly executed corrosion monitoring system providing more precise knowledge on the actual corrosivity that would be available to the wide professional public will help to mitigate losses incurred due to substitution of damaged devices, loss of serviceability, ecological impacts, etc.

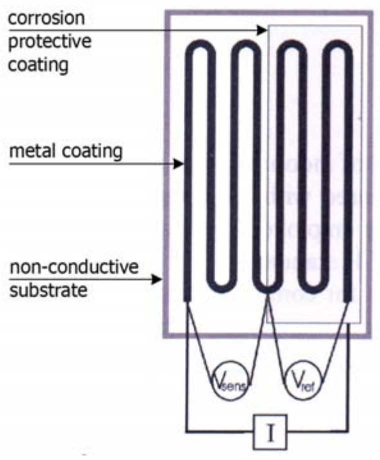
OBJECTIVES

The aim of this project was to develop small, independently working sensor devices for reliable, rapid, and reproducible monitoring of corrosion. It included two dimensions. The first dimension was related to **optimization of the direct accessibility of the data for end-users**, i.e. the minimum need for interpretation and optimized simplicity of communication between the sensor device and the end-user. This part is to a large degree independent of the actual process system in which the sensor is applied (atmospheric conditions, water, soil, etc.). The second dimension was related to the **accuracy and reliability of the sensors** in their individual application platform. The project was focused on development of **indoor and outdoor atmospheric corrosion sensors and fluid or soil media corrosion sensors for internal or external corrosion detection.**

The innovative objectives of the project consisted of:

(1) **High sensitivity and reliability of the sensor device, i.e. short time to respond**;
(2) **Small size for sensors and measuring device and battery driven device**;
(3) **Simple operation demanding no special skills of the personnel**;
(4) **GSM-reading based remote control**; and
(5) **Detection of localized corrosion**.

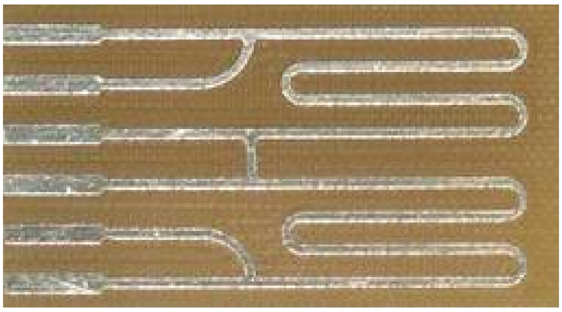
PRINCIPLE



The concept of the measuring device is simple and yet highly effective. The electronic unit measures and registers the changes over time in the electrical resistance of a thin metal track applied on an insulating substrate. If the metal corrodes, the cross-sectional area of the track decreases and electrical resistance increases. In practice, two such elements are built into a probe. One element is exposed to the corrosive environment and corrodes whereas the other element is shielded and thus protected from corrosion. The resistance of both elements is measured at the same time and resistivity changes due to the varying temperature are compensated. Based on the initial cross sectional area of the exposed element, the cumulative metal loss at the time of reading is determined. There is no need to remove the probe from the environment; hence, the technique is online. The technique can be used practically for any kind of environment. Recent developments of the ER technique involving better means for temperature compensation and higher resolution of the resistance measurements have now turned the technique into a (at least semi-) real time technique where the time needed to create sufficiently high increase in resistance has been reduced to hours or even minutes.

CORROSION MONITORING IN ATMOSPHERE

The monitoring system comprises principally of two parts, i.e. corrosion sensor and electronic logger. The corrosion sensors consist of metallic tracks of various thicknesses deposited on a non-conductive substrate using a combination of electroless and electrolytic deposition (ED), printed circuit board (PCB) technique or another technique developed within the project. The width of the measuring track is 1 or 2 mm depending on the application. This geometry ensures high sensitivity to changes in the electrical resistance due to metal corrosion. However, the sensitivity and service life of sensors mainly depend on the thickness of the metallic track. The lower the thickness, the higher the sensitivity. On the other hand, low thickness leads to a shorter service life. The service life can be assessed as the time to consume a half of the thickness of the track. Therefore, sensors with several track thicknesses are available for application in environments of different aggressiveness.



Protection of the reference track against corrosion is provided by a thin organic coating. The coating is transparent to avoid differences caused by heating up of the reference and sensing tracks when irradiated with sun. A polyurethane lacquer was selected from nine tested clear coatings in view of the best wet adhesion and UV stability.

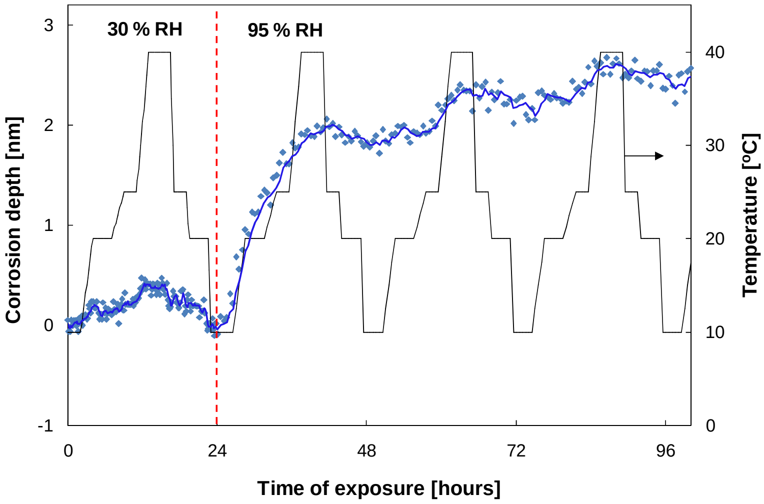
So far, sensors made of iron, zinc, and copper have been developed at several thicknesses for different applications. An overview of developed sensors together with the sensitivity is in the table. Sensors made of nickel, aluminum, stainless steel, and steel at 100 and 250 μm are also available, but the development is not completed yet.

Metal	Thickness [μm]	Application	Sensitivity [nm]
Zinc	1–2	Indoor	3
Zinc	25	Outdoor	11
Iron	25	Indoor	8
Copper	1	Indoor	1
Copper	5	Outdoor	3

The corrosion sensors cannot work without a device that measures the electrical resistance of both the coupon and reference tracks, while also saving data for further processing. The basic version of the CORRLOG logger is encased in a small polycarbonate watertight box with dimensions of 100×65×37 mm and a tightness of IP 65. The logger lid is provided with a watertight connector with a sensor which can easily be replaced when necessary. Furthermore, if the corrosion depth threshold defined by a user is passed, an LED signals that the limit has been exceeded. In addition to these features, the cadence of the measurement can be adjusted from minutes, to hours, to even days if necessary in order to match the sensitivity of the measurement with the anticipated corrosion rate.

Collected and stored data can be transferred to a computer via a non-contact inductive data reader, even through the showcase glass. A GPRS/GSM access unit is an attractive option when the monitoring is carried out at a distant place. It allows for remote data access and control with automatic data delivery via e-mail. Loggers are designed to be autonomous for two to three years and the battery itself is also replaceable. Therefore the loggers are fully independent from any power supply, any external control, and thus can be placed anywhere.

A broad corrosion testing was conducted in order to evaluate the sensitivity and reproducibility of the corrosion depth measurement and response time of the unit while working with different sensors. The corrosion depth measured on a 1 µm thick copper sensor is shown as an example. The low deviation of the signal in dry air was caused by a combination of a measurement error from the electronic logger and temperature changes. After exposure to humidified air, the corrosion depth started to increase rapidly above the level of the electronic and temperature noise. Indeed, the change in atmosphere corrosivity was observable after less than two hours. The sensitivity of the measurement was also tested in identical conditions. The minimal change in the corrosion depth that could be obtained from the data ranges from 1–11 nm according to the type of a sensor. This data confirms that the apparatus is able to respond rapidly to changing climatic conditions with sufficient sensitivity to ensure the integrity of the data.



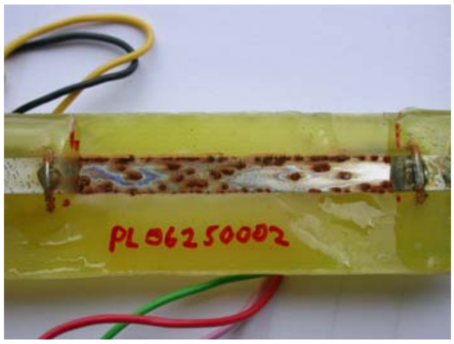
CORROSION MONITORING IN SOIL AND AQUEOUS MEDIA

The development of an **aqueous corrosion sensor** with optimum reliability and sensitivity for the desired end use has been the objective throughout the project. Using knowledge on the ER sensing principle, different geometrical arrangements of sensing elements, and different sealing materials were tested to study the effect of fluctuating temperature and strain on performance. A new testing procedure in non-corrosive media has been developed for this purpose and knowledge on design parameters obtained. Based on the defined acceptance criteria including temperature compensation and sensitivity, two final prototype designs were chosen, one for a flush-mounted probe, and one for an insertion probe. Correlation between electrical resistance responses monitored by the existing logger and the corrosion rate actually occurring on the sensor element was tested in a well-defined laboratory test and found to be in very good agreement. Design specifications based on end-user requirements were identified and a number of insertion steel prototypes manufactured and tested in preliminary field tests. The probes proved to be successful and the results are in agreement with coupons (weight loss) mounted in the same systems.

At the initiation of the project it was discussed how sensor material should be manufactured to best simulate the actual construction material. Based on these results the conclusion is that for the systems in question (geothermal water, district heating water, oil & gas, soil) the difference in corrosion behavior between iron foil and carbon steel is low, and iron foil is a suitable sensor material to fulfill the needs of the end-users. The practical manufacturing of the sensor elements was also studied and the final recommended technique is the use of metal foils. Chemical or electrochemical plating was also studied e.g. for zinc-iron samples, but strong limitations on sensitivity could be the result, as the electrical resistivity of plated layers are in some cases extremely high. Machining of samples to low thickness also turned out to be unsuitable and inpractical.

So in practice the sensitive pipeline prototype sensor designed in this project for energy systems (oil, gas, geothermal water) is sensitive to changes in corrosion rate, but not too sensitive to temperature fluctuations, and iron foil is an adequate material to be used for the corrosion sensors used in this industry. The insertion probe is now available at Metricorr and will be marketed for district heating water applications primarily. The flush-mounted probe can be manufactured on request.

Drinking water installations are in Denmark typically made of hot dip galvanized steel, which is inexpensive and has a reasonable lifetime. Corrosion failures however do occur and often after only a very short exposure time. Development of a flush mounted zinc probe for simulating hot-dip galvanized steel included evaluation of the most suitable material in terms of corrosion resistance and practical possibility of using the material for an ER probe. Flush probes were manufactured in pure zinc foil, iron and electroplated Zn-Fe alloy probe elements. The probe was easily mounted in the existing potable water system, simulating a piece of pipe. Studies in hot potable water with and without corrosion inhibiting system included monitoring of corrosion rate, scale formation, micro-structural characterization of the sensing elements and cross sectioning so as to correlate true corrosion rates (thickness reduction) with ER data. The result is that hot dip galvanized steel in hot potable water is well simulated by pure zinc foil and that the flush design functions well.



In this work an already patented idea (Metricorr) was incorporated. This idea makes it possible to monitor formation of protective scale and corrosion rate simultanously. This is a strong tools for e.g. providers of corrosion protection systems, who can optimise their protection and document its function. Another already patented idea on measuring electrochemical parameters were also tested for these systems, and gave useful information on corrosion status for especially the more trained personnel. The data treatment is incorporated in the available software from Metricorr. The Metricorr logger was at the start of the project already in function, but has during the course of the project been adjusted and optimised to implement knowledge gained in the project. Traditionally it was developed for cathodically protected pipelines, but the changes makes it suitable for all systems, where the potential measurement option can be used to follow open circuit potential, and the spread resistance option to follow scale formation.

One of the major limitations is the inability to trust the corrosion rate data if localized corrosion occurs. It is therefore of importance to identify, if non-uniform corrosion is active, and if possible to get an estimate of the degree of attack. A survey has been initiated on the possibility of developing a non-uniform corrosion sensor, based on ER-technique. End-user tests, where failure of sensors due to localized attacks were observed, have been used as inspiration. A series of tests have been developed to investigate the characteristics of non-uniform vs. uniform corrosion. Different probe geometries and different measurement principles have been investigated and promising results obtained, which indicate that discrimination could be possible. The development process is however not finalized and no direct results can be revealed without impairing the chance of patenting. The results will be included in further research and development.

MAIN CHARACTERISTICS OF END PRODUCTS

Atmospheric corrosion logger: (1) Lifetime in medium-corrosive environments of about 2 years with full autonomy in terms of thickness of the sensing metal layer, data capacity, and battery lifetime; (2) Size of 100×65×37 mm and weight of 180 grams for the logger without GPRS reading; (3) Watertight box with a tightness of IP 65; (4) Available with zinc, iron, and copper sensors at thickness from 1 to 25 µm; sensors made of other metals are under development; (5) Sensors are easily exchangeable; (6) The sensitivity of measurement from 1 nm; (7) Optional GPRS access unit allows automatic data transfer by e-mail and distant programming.

Aqueous corrosion sensor: (1) Approximate size of the logger is 25×50×100 mm; (2) Available with zinc and iron sensing part, but other metals may be used if available as thin foils; (3) Sensitivity of 10 ppm of the element thickness; (4) Time to respond from 15 minutes to 2 hours depending on corrosion rate; (5) Isolating scale formation can be monitored as the so-called spread resistance; (6) Optimized (higher sensitivity and less temperature disturbance) design for flush or insertion probe available; (7) The option to monitor the presence of non-uniform corrosion in real time is under development and may in future be integrated in the product.

AREAS OF SENSOR APPLICATION AND AVAILABILITY

The sensors developed within the scope of the CORRLOG project will be applicable in various fields where monitoring of corrosion is vital:

- *Industry*. Monitoring of e.g. addition of corrosion inhibitors and biocides in cooling water, corrosivity of district heating water, geothermic water, and hot potable water supply.
- *Cultural heritage*. Actual information on the corrosivity of atmosphere will allow taking rapid countermeasures in order to protect indoor and outdoor objects of cultural heritage.
- *Pollution monitoring*. The sensor can be used as an early pollution detector for different pollutants such as ozone, SO_2, NO_x and H_2S, depending on the selection of metals sensitive to these gases. The sensor would be useful if applied for on-line monitoring at locations with dangerous pollution, such as industrial plants.
- *Transport and storage*. Monitoring of corrosivity during transportation and storage of goods, and better management of corrosion protection of ships and vehicles.
- *Civil engineering*. Monitoring of the corrosivity of structures and materials used in the civil engineering will facilitate selection of proper materials for given applications.
- *Electronics*. Monitoring of the corrosivity of sensitive electronics for different applications such as GSM stations, control rooms, or on-board electronic equipment in vehicles and ships.
- *Oil and gas industry*. The main field of application of the aqueous corrosion monitoring system. Oil and gas transport, storage, processing, and distribution.

Extensive testing by end users formed an important part of the project. The partners in the testing were the Prague Castle and National Museum in Prague, Czech Republic, National Museum of Denmark, Swiss National Museum, C2RMF France, DGA, France, Volvo Car Company, Sweden, City of Naples, Italy, Hovedstadsregionens Naturgas, Søborg and Hadsten Varmevaerk, Denmark, and others.

The logger for corrosion monitoring in air will be commercially available in the end of 2008. The aqueous corrosion logger is already available and can be purchased from MetriCorr.

PARTNERSHIP AND CONTACTS

The project brought together three enterprises from France, Denmark, and the Czech Republic. All of them are well established in their fields, i.e. electronics and software development, corrosion engineering, and metal deposition. An important part of the research and development was carried out by two technical universities. The work was coordinated by Institut de la Corrosion.

Institut de la Corrosion
French Corrosion Institute
220 rue Pierre Rivoalon,
29200 Brest, France
www.institut-corrosion.fr
Dr. Dominique Thierry
Phone: +33 298 058 901
dominique.thierry@institut-corrosion.fr

nke
Rue Gutenberg, Z.I. Kerandré
56700 Hennebont, France
www.nke.fr
Mr. Yves Degres
Phone: +33 297 361 012
ydegres@nke.fr

INSTITUTE OF CHEMICAL TECHNOLOGY PRAGUE
Technická 5, 166 28 Praha 6, Czech Rep.
www.vscht.cz/met
Dr. Milan Kouřil
Phone: +420 220 443 750
milan.kouril@vscht.cz

GT Galvanotechna
468 04 Jablonec nad Nisou, Czech Rep.
www.galvanotechna.jn.cz
Mr. Vratislav Blažek
Phone: +420 483 710 356
galvanotechna@jn.cz

Danmarks Tekniske Universitet DTU
Dept. of Manufacturing Engineering and
Management, Kemitorvet, Building 204
DK-2800 Kgs. Lyngby, Denmark
www.dtu.dk
Dr. Lisbeth Rischel Hilbert
Phone: +45 45 25 21 93
lrh@ipl.dtu.dk

MetriCorr
Produktionsvej 2
DK-2600 Glostrup, Denmark
www.metricorr.dk
Dr. Lars Vendelbo Nielsen
Phone: +45 72 17 74 06
lars.vendelbo.nielsen@metricorr.dk