SensCorr™

Corrosion Monitoring

Scientific Manual

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Content

1 Introduction

The SensCorr is an instrument for corrosion monitoring and electrochemistry. It contains an instrument for doing electrical resistant measurements and a fully programmable potentiostat.

We supply the SensCorr with three interfaces:

1. 4-20 mA HART. This is *the* digital interface for the industry. All data are transmitted digitally through the 4-20 mA analogue loop standard, which since the 1950's has been *the* industrial standard for transmitting data. The instrument is powered by this loop (at 24 Volt). This interface is for the industry, the oil and gas, geothermal and all other places where 4-20 mA (sometimes) is available, like in buried pipelines. The HART instrument is the HART Loop Converter.
2. 4G wireless interface to 'the cloud'. This is for standalone instruments, as used for civil engineering projects like bridges or buried pipelines. One battery lasts more than a year but normally solar cells are connected which makes lifetime >25 years. This instruments is for standalone situations, like civil structures and buried pipelines.
3. Data logging on an SD card. This is for scientific and laboratory purposes. But also for all other locations for temporary 'trials'. The battery lasts > 1 year.

The SD datalogging card can be combined with 4-20 mA HART or 4G wireless in the cloud.

This manual will explain how the instrument works and it will show the calculations behind the measurements.

2 Electrical Resistance Measurements (ER)
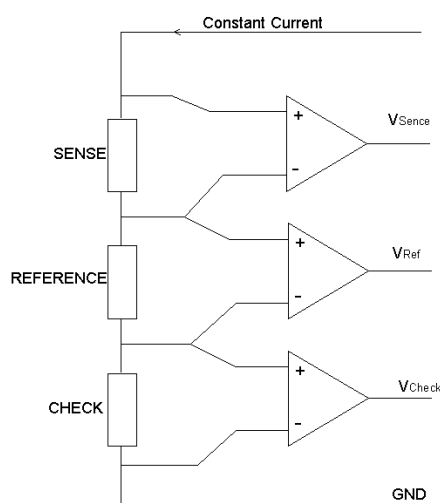
Electrical Resistance (ER) measures the resistance of an exposed element compared to a embedded reference element.

Electronic Circuit of ER measurement.
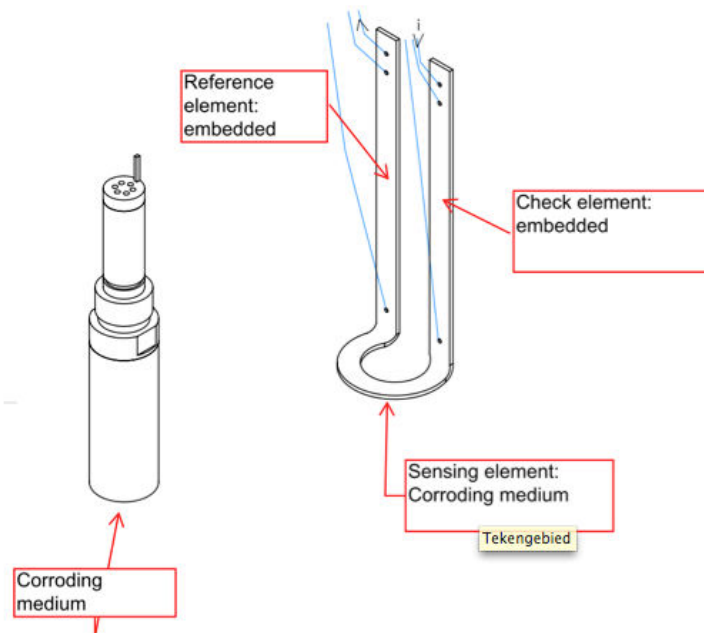
Strip ER element. A current is sent through the strip and four sensing elements pick up the Voltage drop.

The metal loss is calculated as follows:

Ratio = R-reference / R-exposed

Metal loss = (Original thickness of element) minus (Ratio times original thickness of element)

Normally an element thickness of 500 micrometer is used. The sensitivity in that case is about 1 micrometer. A thickness of 100 micrometer results in a sensitivity of 0,1 micrometer.

The value 'metal loss' is logged by the SensCorr and/or sent to the HART Loop Converter.

Logged are:

1. Original thickness of the element in micrometer
2. Ratio
3. Metal loss in micrometer

3 Electrochemistry

3.1 Galvani, Volta, Ampère, Ohm's Law and Faradays Law

In the late 18th century the Italian physician and anatomist Luigi Galvani marked the birth of electrochemistry by establishing a bridge between chemical reactions and electricity on his essay *"De Viribus Electricitatis in Motu Musculari Commentarius"* (Latin for Commentary on the Effect of Electricity on Muscular Motion). In 1791 he proposed a *"nerveo-electrical substance"* on biological life forms. Based on Galvani's experiments, Alessander Volta invented the battery in 1800. The ampere is the unit for current, it is one of the seven basic units of the seven quantities of the SI system. It was called after André-Marie Ampère, (1775-1836), one of the main inventors of electromagnetism. Ohm's law states that the current through a conductor between two points is directly proportional to the voltage across the two points (1827).

Or:

$U = I * R$

U = Voltage in V
I = Current in A
R = Resistance in Ohm

In electrochemistry the Voltage is called a 'potential' with the quantity E and the unit mV. Current is normally expressed in current density of mA/cm^2.

In fact Volta also invented electrochemical corrosion because a battery is electrochemical corrosion. For a battery you need three things:

1. A cathode. For example this is steel (iron).
2. An anode. For example this is zinc.
3. An electrolyte in which the anode and cathode have been submerged.
   An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. For example this is aerated seawater.

If the anode and cathode are isolated one from the other, a Voltage of about 0,5 Volt is given.
The anode and cathode need to be connected with an resistor one to the other in order to make an electrical current (in Amperes) possible. This is the current that the battery delivers.

At the cathode the following reduction reaction occurs: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

At the anode the following oxidation reaction occurs: $Zn \rightarrow Zn^{2+} + 2e$

The anode is where the electrons enter the electrode and the cathode is where the electrons leave the electrode. In case of zinc, two electrons cause the dissolution of one zinc atom. The laws, which govern the deposition of substances (In the form of ions) on electrodes during the process of electrolysis, is called Faraday's laws of electrolysis. These laws were given by Michael Faraday in 1833.

Faraday's first law: It states that,

"The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed."

Thus, electrochemical equivalent (ECE) may be defined as "the mass of the ion deposited by passing a current of one Ampere for one second (i.e., by passing Coulomb of electricity (electrons))". It's unit is gram per coulomb.

The coulomb (symbol: C) is the International System of Units (SI) unit of electric charge (=electrons). Under the 2019 redefinition of the SI base units the coulomb is the charge of $6.2415090744 \times 10^{18}$ electrons or 1.036×10^{-5} mole electrons (elementary charges). This was discovered by the French scientist Charles-Augustin de Coulomb (1736-1806) .

1 Coulomb is 1 As (ampere*second). This is the charge of 1 A during 1 second. Knowing the number of electrons in one coulomb, the metal loss weight of a current density can be calculated. Knowing the weight loss over time and the surface of the electrode, the corrosion rate in mm/year can be calculated.

3.2 Corrosion

Corrosion can be a chemical reaction, normally high temperature corrosion, or an electrochemical reaction with an electrolyte. An electrolyte is a conductive fluid, normally water. Electrochemical is the process that causes corrosion in industry, the atmosphere, buried pipelines, concrete steel and so on. By far steel (iron) is the metal that is involved in these markets. At ambient temperatures corrosion will not occur if an electrolyte is absent. In the atmosphere a relative humidity of >80% is required for making (significant) corrosion possible. Always two reactions must occur simultaneously:

1. The anodic reaction that releases electrons to the metal.
2. The cathodic reaction that subtracts electrons from the metal.

For example for corrosion of mild steel in aerated water:

Anodic oxidation reaction: $Fe \rightarrow Fe^{2+} + 2e$

Cathodic reduction reaction: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

In an acid the following cathodic reaction occurs: $2H^+ + 2e \rightarrow H_2$

3.3 Electrodes

For electrochemical measurements three electrodes are used:

The reference electrode RE

This is the reference on which a potential (mV) between the working electrode and the reference can be set. If the reference is an Ag/AgCl electrode, the rest potential compared to steel is about -500 mV. Ag/AgCl electrodes are widely used for laboratory and field measurements because their noise level is very low.

Corrosion monitoring electrodes are made of similar alloys, normally carbon steel. Also electrodes made of stainless steels, copper and all other metals and alloys are possible. If carbon steel is the metal that is being investigated, it means also the reference is made of the same carbon steel, which results in a very robust reference, compared to the Ag/AgCl reference electrode.

The disadvantage of using carbon steel is that the noise level of a steel reference electrode is higher than the noise level of a Ag/AgCl reference electrode. But for linear polarization measurements and E-log I scans this normally is not a problem. For corrosion monitoring, steel reference electrodes are recommended and for laboratory setups Ag/AgCl reference electrodes are recommended.

When you measure a potential, always the reference electrode must be mentioned. For example: the cathodic protection limit according to NORSOK B401 is -800 mV Ag/AgCl. For steel the notation in this case is -300 mV St.

The working electrode WE

The working electrode has been made out of the alloy that is being investigated. Normally carbon steel is used. Between WE and RE the potential is measured in mV. WE is polarized by an electric current that is supplied by the counter electrode.

The counter electrode CE

The counter electrode makes polarization of the working electrode possible. This can be with a cathodic current, in the minus direction, or with an anodic current, in the positive direction.
In laboratory setups often platinum counter electrodes are used. But for the SensCorr potentiostat the counter electrode always must be made out of the similar material compared to the working electrode, because for corrosion monitoring the electrodes all three are made of a similar alloy. For laboratory setups the reference can be an Ag/AgCl reference or other reference if required.

Three electrodes in reinforcing steel: RE (in the middle) and WE and CE. The steel strip is the ER element.

3.4 Potentiostat

The potentiostat is the instrument that makes the electrochemical measurements possible. It's an instrument that can be set to a fixed potential compared to the reference electrode. For example it can be set to a potential of -50 mV St.. Normally cathodic and anodic scans are made. For example a cathodic linear polarization scan compared to a carbon steel reference of 0- -25 mV St. and an anodic linear polarization scan of 0- +25 mV St. with a scan rate of for example 1 mV/second. Also full polarization scans are made: For example -800 mV Ag/AgCl to -200 mV Ag/AgCl at a scan rate of 0,1 mV/s.
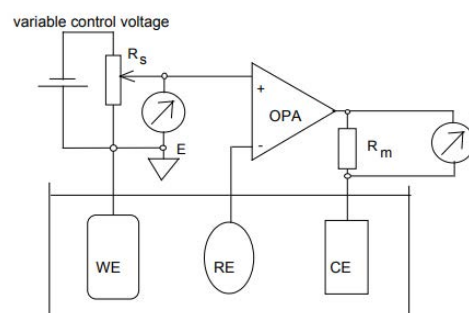
Basic scheme of a potentiostat: Dr. Rudolph Dölling, Bank Elektronik.

Programmable potentiostat with an electrochemical cell containing seawater with the three electrodes: Working electrode (carbon steel), AgCl reference electrode and a counter electrode.

4 Programs Electrochemistry

4.1 Electrochemical Noise and Linear Polarization Resistance

Basic theory ECN

An electrode is polarized as caused by local corrosion. Meaning the potential will be for example 10 mV. As caused by corrosion, a film will develop and cause an increase of the potential to the original value. This is the electrochemical noise. If two electrodes have a potential difference of 10 mV, a current will run once the electrodes are connected through a resistor.

The SensCorr can measure both potential between WE and RE, and current between WE and CE.

ECN is very much suitable for measuring the performance of corrosion inhibitors. Also ECN can be used for measuring the likelihood on localized corrosion (pitting and stress corrosion cracking) compared to uniform corrosion. According to ASTM G199, from the noise data, information on pitting corrosion is obtained by three methods: pitting index, pitting factor, and pit indicator or coefficient of variation.

4.2 Potential noise E-noise (measured) ASTM G199

Two values are logged:

1. Maximum E-noise in mV.
2. Mean E-noise in mV.

The mean noise can be set as a floating B-value for the LPR calculations.

4.3 Current noise I-noise (measured) ASTM G199

Localized corrosion (pitting corrosion, environmental cracking).

$$Pitting\ Index\ PI = \frac{\sigma - I}{I - rms}$$

Where:
I rms = the root mean square of the current noise
σ I = the standard deviation of current noise

In mathematics and its applications, the root mean square (RMS or rms) is defined as the square root of the mean square (the arithmetic mean of the squares of a set of numbers). The RMS is also known as the quadratic mean and is a particular case of the generalized mean with exponent 2. RMS can also be defined for a continuously varying function in terms of an integral of the squares of the instantaneous values during a cycle.

The values of PI range between 0 and 1. Values of PI above 0.6 may indicate localized corrosion.

Five values can be logged or sent to the HLC.

1. Maximum I-noise in micro A/cm^2
2. Mean I-noise in micro A/cm^2
3. Pitting Index PI
4. Corrosion rate in mm/year calculated from I-noise mean according to Faradays Law and ASTM G59 (see LPR calculations).
5. Corrosion rate in mils (milli inches per year).

4.4 LPR measurements according to ASTM G59

Linear Polarization Resistance (LPR) measurements have been widely used since the 1930's. They have been standardized according to ASTM G59.

In order to make the cathodic / anodic region as accurate as possible, scans are made from the measured mean potential noise value (this is defined as 0 mV St.). In order to

avoid deviations because of the noise of RE, scans are made at high speed. Current is measured after 0,1 second succeeding delta E has been achieved.

With the potensiostat a scan can be made from the rest potential in the negative (cathodic) and positive (anodic) direction. For steel the rest potential (also mentioned the corrosion potential) is about -500 mV Ag/AgCl. For a carbon steel reference the rest potential of course is about 0 mV St.. Suppose the anodic and cathodic scan are made from 0 mV St. -/+ 25 mV St. with a scanrate of 10 mV/s.

Ohms Law says: **Rp = E / I**

E= potential in mV
I = current density in mA/cm^2
Rp= linear polarization resistance in Ohm.cm^2

In case of a cathodic scan of -25 mV St. at 0,1 mV/s, the minimum potential is taken (-25 mV).

Rp = ΔE/I

If I = -0,01 mA/cm^2, Rp = -25/-0,01 = 2500 Ohm.cm^2
Also an anodic scan can be made. For example Rp for the anodic scan is 1670 Ohm.cm^2. The highest resistance cathodic/anodic is valid for the calculation of the corrosion rate because this resistance limits the corrosion current. In this case this is 2500 Ohm.cm^2.

B is a constant in V

$$B = \frac{ba*bc}{2.303*(ba+bc)}$$

The units of the tafel slopes are Volt. ba is the anodic tafel slope and bc is the cathodic tafel slope. B can be determined with laboratory experiments. For the calculations B is in mV.

For water B normally is 26 mV.

Icorr = B / Rp

Icorr = the corrosion current density in mA/cm^2
B is a constant in mV
Icorr = 26 / 2500 = 0,01 mA/cm^2

According to Faraday's Law:

$$CR = 3{,}27 \frac{Icorr * EW}{\rho}$$

CR is the corrosion rate in mm/year.
EW is the equivalent weight. For Fe^{2+} this is 56/2 = 28 grams/mol.
ρ is the density. For steel this is 7,8 grams/cm^3.

$$CR = 3{,}27 \frac{0{,}01 * 28}{7{,}8} = \textbf{0,036 mm/year}$$ this is **1,4 mils** (milli inch/year).

This value is logged by the SensCorr and sent to the HART Loop Converter.
Note. Experiments showed that using potential noise values give more realistic values of B. The SensCorr also can be set at this B-value, that is measured real-time. Two B values can be set with the SensCorr:

1. B-constant (normally 26 mV)
2. B= Mean E-noise

The following data are logged:

Cathodic lpr scan:

1. A (surface) in cm^2
2. ΔE in mV
3. I-polarization (= i-measured) in mA/cm^2
4. Rp in Ohm.cm^2

NOTE: By setting ΔE to the right value, the oxygen content can be measured semi-quantitatively.

Anodic lpr scan:

1. A (surface) in cm^2
2. ΔE in mV
3. I-polarization (= i-measured) in mA/cm^2
4. Rp in Ohm.cm^2

The time between cathodic and anodic polarization scan can be set. Typically this is 20 minutes.

Corrosion rate calculations out of Rp max (cathodic / anodic):

1. B-constant or B (mean potential noise), upon choice.
2. I-corrosion in mA/cm^2
3. EW in grams/mol

4. ρ (density) in grams/cm^3
5. Corrosion rate in mm/year
6. Corrosion rate in mils (milli-inches/year)

4.5 Current noise (calculated) ASTM G199

Knowing the potential noise and the maximum (cathodic/anodic) value of the lpr resistance, the noise (mean, maximum, etc.) also can be calculated from:

$$\text{i-noise(calculated)} = \frac{E-noise}{Rp(\max)}$$

In the same way, the pitting index PI can be calculated.

Localized corrosion (pitting corrosion, environmental cracking).

$$Pitting\ Index\ PI = \frac{\sigma - I}{I - rms}$$

Where:
I rms = the root mean square of the current noise
σI = the standard deviation of current noise

The values of PI range between 0 and 1. Values of PI above 0.6 may indicate localized corrosion.

Five values can be logged or sent to the HLC.

1. A in cm^2
2. Maximum I-noise in micro A/cm^2
3. Mean I-noise in micro A/cm^2
4. Pitting Index PI

4.6 Electrochemical scans

A full polarization scan from cathodic to anodic referred to E-rest.

A full polarization scan from cathodic (e.g. -900 mV E-rest) to anodic (e.g. + 300 mV E-rest). Because the settings are from E-rest, the SensCorr automatically recognizes the reference electrode.

The scan rate is adjustable. Typically this is 0,1 mV/s
The log rate is also adjustable. Typically this is 1 sample/second

Logging:

1. Potential in mV
2. Current in micro A

Data presentation and MS Excel

The data are presented in a csv (excel) file. The polarization graph can be made with MS excel where the current is on a logarithmic scale.

Below a scan (blue line) from -900 to -350 mV. Steel (WE) and AgCl (RE) in water. The logging rate of the scan can be chosen.
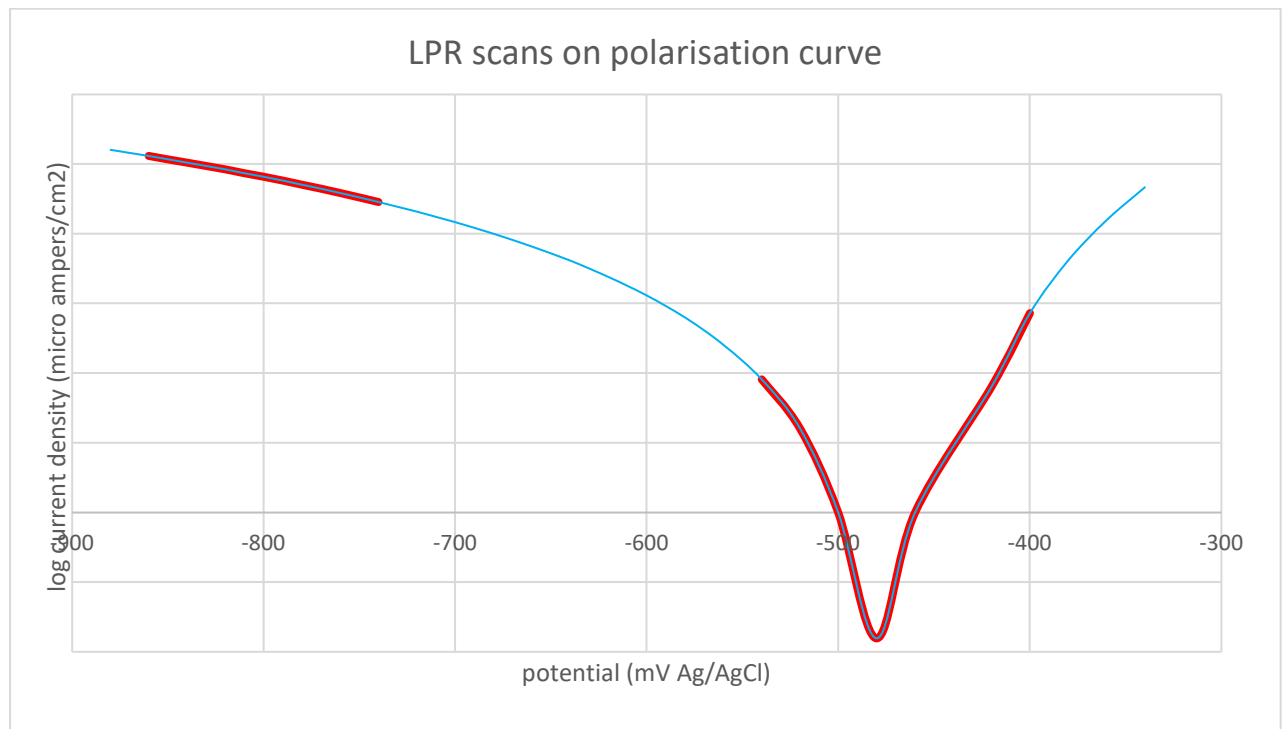
Graph 1: LPR scans on polarization curve (blue line). The red lines: Right a normal lpr scan with anodic and cathodic current and left a lpr scan under cathodic protection of the working electrode.

4.7 Measuring cathodic reduction reactions

For example with a polarization scan according to par. 4.2, the cathodic reduction reaction can be measured at a particular potential. This may be the reduction of oxygen and water to OH^- or reduction of H^+ to H_2. But also rare reduction reactions, like in the very salt Geothermal water, are detected.

Reactions current logging / HART Loop Converter
Once experiments from the scan (par 4.2) show a corrosion reaction at a certain potential, this potential can be set and the current belonging to it is logged and can be sent to the HLC.

This is very interesting for Geothermal because this water appears to show very rare corrosion reactions.

The following is logged and can be sent to the HLC:

1. E-reaction
2. Current belonging to E-reaction

4.8 AC current

Worldwide conductivity of electrolytes is measured with AC currents.

The transition layer metal/electrolyte can be explained as a parallel connected resistor and capacitor. This implies that the resistance of the electrolyte (for example concrete) can be measured with an AC current because a capacitor conducts AC currents.
The data can be used for a correction of the lpr resistance to even a more accurate value. The resistance of some electrolytes, like concrete, may provide more information about the condition of the concrete itself. Still this has to be further worked out by using more practical measuring data.

The SensCorr logs the specific resistance in Ohm.cm^2.

5   Cathodic Protection (CP)

5.1 General

Steel can be protected by cathodic protection if it has been submerged in the electrolyte (water, soil, concrete) and if the surface of the steel and volume of the electrolyte are significant. Often this is combined with coatings, such as for ships and buried pipelines. But for example offshore platforms and offshore windmills are successfully protected uncoated for >30 years without any sign of corrosion.

For cathodic protection a protection current needs to be delivered. This can be achieved by sacrificial anodes (zinc, aluminium or magnesium for fresh water), the battery of Volta, or by impressed current with a potentiostat. Normally seawater protection is done with sacrificial anodes and protection of buried pipelines and tanks (protection in soil) is done with impressed current. For environmental reasons, more and more impressed current is used for seawater and brackish water. Like with harbors (quay sheets and piles) and offshore windmills.
By delivering a current (electrons) to the cathode (the steel under protection), the potential will drop with about 300 mV to -800 mV Ag/AgCl. This is also the limit value according to NORSOK RP B401. The current is delivered by the anodes, either sacrificial anodes or titanium anodes with a coating.

Also buried pipelines (with a coating) are protected successfully. Interference of AC currents, caused by high Voltage power lines is an issue nowadays and the SensCorr can help to solve these problems by telling whether, and how, the CP system on that place needs to be adapted.

Reinforcing concrete steel also is protected by CP but typically on places with a high load of road salts. For example bridges in Scandinavia and the Alps.

5.2 CP measuring

Nowadays often ER probes are used for measuring the CP performance of buried pipelines. The SensCorr measures ER up to a sensitivity of 0,1 micrometer metal loss.

For electrochemistry, cathodic protection performance easily can be measured with the SensCorr by connecting the working electrode to the object under protection. This is done via the enclosure through a cable from this object to the enclosure. In this way the rest potential Ecp is measured between WE and RE (both made of carbon steel). Normally Ecp is -300 - -500 mV St.. Silver/silverchloride or Copper/coppersulfate electrodes are the standard for CP measuring. The SensCorr can (automatically) use these electrodes as reference electrode.

After, the object is disconnected from WE and the current belonging to Ecp is measured. See graph 1. This current, knowing the surface of the electrode, is the

current density of the CP system. The current density is very much depending on the formation of a (protective) calcareous layer on the steel surface.

The formation of this calcareous layer cannot be simulated in a laboratory. Because of the development of this complicated calcareous layer, modelling cathodic protection with finite element software, without measuring on site the CP current density, is absolutely impossible.

Four parameters are logged:

1. ER metal loss in micrometer.
2. The CP potential compared to the steel reference in mV. For a Ag/AgCl reference electrode, this typically is -800 mV Ag/AgCl.
3. The CP current density in mA/cm^2.
4. E-corrosion. A scan is made in the positive direction. Where the current reverses from negative to positive, is defined as E-Corrosion.

6 Microbial Influenced Corrosion (MIC)

6.1 General

The first evidence of life on earth dates from 3,5 billion years ago. These were bacteria. We can assume that MIC already exists for more than a billion year. MIC, caused by a very complex biofilm, is promoted by anodic polarization as caused by an aerobic biofilm. Such bacteria promote the following reaction:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$
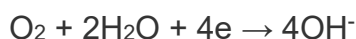
This reaction subtracts negative electrons from the metal. Meaning the rest potential will increase. The metal is polarized in the anodic direction.

For carbon steel this is not really that much a problem. Normally the corrosion rate increases with 5 or 10%. Sometimes, for example with sheets and pilings in harbor quays or in carbon steel firefighting pipes, more MIC is noted. But it must be said. Many carbon steel firefighting pipes in buildings etcetera are >30 years old.

6.2 Stainless steels

For stainless steels, anodic polarization may lead to an exceeding of the so called 'pitting potential', that leads to pitting corrosion. Because of this pitting corrosion, iron ions are released. It leads to the formation of iron related bacteria (IRB's) in the biofilm. Such bacteria attract sulfate reducing bacteria (SRB's) and acid producing bacteria (APB's). These bacteria are anaerobic, meaning they will settle below the aerobic biofilm, on the metal surface. Together with chlorides in the water hydrochloric acid forms below the biofilm on the metal surface. In other words, MIC can be very corrosive for stainless steels, which also implies that the higher the chloride content, the higher the risk on MIC of stainless steels.

Examples are known that new stainless steel 316 firefighting water lines were leak within half a year because brackish harbor water (meaning full of microbial life) was left in the pipes after a pressure test. This happened during the summer, meaning the MIC risk is high because of the relative high temperature. MIC and Legionella both are a biofilm problem and very much temperature dependent. Not the MIC on itself is the problem, the biofilm growth at relatively high temperature is the problem.

Another example is a nuclear institute for proton therapy in a hospital. New stainless steel 316 cooling water pipes with demands for highest purity of the water showed MIC prior to the commissioning of the therapy facilities. These stainless steel pipes were installed in a meter thick concrete walls and MIC was caused succeeding pressure testing with tap water.

6.3 SensCorr MIC measuring

Pitting corrosion of stainless steel

The SensCorr can measure MIC with a normal lpr measurement according to ASTM G 59. The linear polarization resistance of the anodic scan is influenced by the corrosive biofilm.

Suppose you want to measure MIC of super duplex steel SAF 2507 in seawater (full of microbial life) at 30 ºC, all three electrodes are made of this material. In order to avoid crevice corrosion, the embedded part of the electrodes has to be fabricated of carbon steel. The biofilm will form on all three electrodes, meaning, the rest potential will remain near 0 mV compared to a RE in SAF 2507. In the absolute value the potential rises as caused by the aerobic biofilm. Relatively, compared WE to RE, this is not the case. Once the pitting potential is (almost) reached, the anodic lpr value will decrease because of pitting corrosion.

7 Environmental cracking of stainless steels / coupons
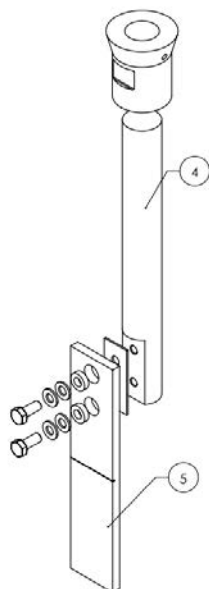
Similar to pitting corrosion, also environmental cracking of stainless steels and other alloys easily can be detected with a normal anodic LPR scan according to ASTM G59. But the working electrode must be pre stressed by cold work and it must be provided with a notch. A cold worked coupon with a notch is used in order to make further investigation in a lab possible once the SensCorr detects a decrease of the anodic polarization resistance. Also the working electrode itself can be analyzed in the lab in this way. On the left an example of a super duplex SAF 2507 lpr probe with a pre stressed coupon with a notch, in a super duplex flow line at 380 bar and 95 ºC. This was for natural gas with produced water at extreme high salinity at a pH value 3.6 and high hydrogen sulfide content.

It's also possible to make this coupon as working electrode, meaning, this is an 'electronic coupon'. In that case, the embedded part of the coupon must be made of carbon steel in order to avoid crevice corrosion.

8 pH and temperature measurement

The SensCorr ER + motherboard contains 4 slots for modules:

1. Progammable potentiostat.
2. Interface (HART or G4 radiographic).
3. Interface SD card datalogging.
4. A vacant module slot, e.g. for pH and temperature measurement.

NOTE: Also a second programmable potentiostat can be inserted in the vacant slot.

9 Electronic Testprobe

The SensCorr is provided with an electronic testprobe for testing functionality of ER and LPR. This is a 'program' that can be set with a dipswitch.

Logged are:

1. ER ratio
2. LPR value in mm/year

10 HART Loop Converter

The HART loop converter has 4 digital channels: pV, sV, tV and qV. Three analog 4-20 mA output channels are available. With push buttons the digital channels can be appointed to the analogue channels.

All data that are logged, as mentioned above, can be sent to the 4 available channels.

Via one channel many parameters can be appointed. For example 5 parameters alternatively via one channel every 30 minutes. Normally the 4 digital channels are appointed by one parameter each.

11 SD Data logging

Each SensCorr is provided with a SD datalogging card. Each program results in a report in a csv file format.